

COUPLING THE EFFECTS OF DISSOLVED ORGANIC MATTER AND NUTRIENT
STOICHIOMETRY WITH NUTRIENT UPTAKE IN BOREAL FOREST
HEADWATER STREAMS

By

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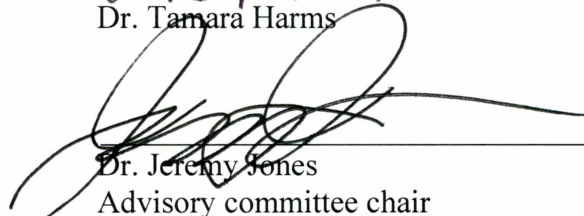
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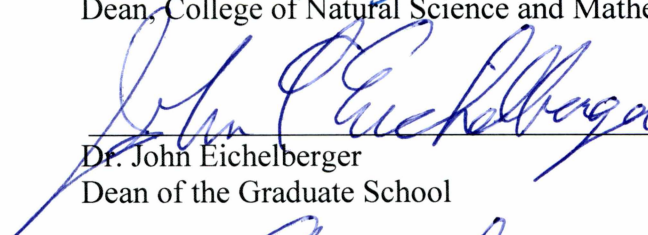


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A
THESIS

Presented to the Faculty
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By

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Abstract

Discontinuous permafrost affects the hydrology and distribution of vegetation in boreal forest watersheds, which in turn influence stream water chemistry. I investigated how loss of discontinuous permafrost with projected climate change might affect nutrient cycling in boreal forest headwater streams. I hypothesized that 1) the carbon, nitrogen, and phosphorus (C:N:P) ratio in dissolved organic matter (DOM) affects nutrient uptake due to stoichiometric constraints on autotrophic and heterotrophic nutrient assimilation, and 2) labile DOM affects nutrient uptake by increasing heterotrophic production. I tested my hypotheses using a series of instantaneous nutrient additions in nine headwater streams, with a factorial design manipulating both nutrient stoichiometry and DOM source. DOM was added as either acetate or leachate from birch leaves. Ambient nutrient uptake velocity (V_{f-amb}) was within the upper range of previously published literature values, ranging from 4.1 – 67.2 mm/min for N, 4.0 – 25.0 mm/min for P, and 4.2 – 34.5 mm/min for acetate. Uptake efficiency was similar for N and P added alone, in co-additions, and with DOM. Acetate and birch-DOM had similar effects on nutrient uptake, because both were sources of highly labile carbon. In 30-day laboratory bioavailability assays, birch and acetate-DOM exhibited $\geq 70\%$ carbon loss. V_{f-amb} was in part explained by ambient stream chemistry, with V_{f-amb} for N weakly positively correlated with ambient P concentration, while V_{f-amb} for P and acetate was weakly negatively correlated with ambient N and ambient dissolved organic carbon, respectively. Consequently, inorganic nutrient availability may affect uptake of solutes as well as DOM lability. High demand for nutrients in boreal forest headwater streams suggests that uptake could increase concurrently with greater inorganic nutrient flux following a loss in permafrost extent.

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Chapter 1: Introduction

1.1 Discontinuous permafrost

Permafrost extends over approximately 25% of the terrestrial northern hemisphere and is defined as subsurface material that is colder than 0°C for a minimum of two years (Permafrost Subcommittee 1988, Zhang et al. 1999). Globally, approximately 50% of belowground carbon is stored in permafrost soil (Tarnocai et al. 2009), making northern latitude soil an important component of the carbon cycle as warming climate affects the distribution of permafrost. The boreal forest of interior Alaska is underlain by discontinuous permafrost, which influences the depth of hydrologic flowpaths through watersheds (Jones and Rinehart 2010) and consequently affects solute transport to streams (MacLean et al. 1999, Kawahigashi et al. 2004).

Discontinuous permafrost in interior Alaska is especially vulnerable to thaw because its temperature is just below freezing (Jorgensen et al. 2010).

In the region of discontinuous permafrost, south facing slopes tend to be free of permafrost, whereas extensive permafrost is found below cold valleys and north facing slopes (Viereck et al. 1983). Catchment vegetation follows the distribution of permafrost, with black spruce (*Picea mariana*) growing in areas of permafrost and deciduous species such as birch (*Betula neoalaskana*) and aspen (*Populus tremuloides*) growing where permafrost is absent (Viereck et al. 1983). The distribution of vegetation is important because forested headwater streams are highly influenced by terrestrial inputs of organic carbon and nutrients from catchment vegetation (Fisher and Likens 1973, Bengtsson and Torneman 2004). At high latitudes a low angle of solar incidence can limit in-stream primary productivity; thus, heterotrophic, rather than autotrophic, processes should dominate nutrient cycling in boreal forest headwater streams (Betts and Jones 2009).

1.2 Nutrient spiraling in streams

Nutrient cycling in streams is conceptualized as a spiral because advection is constantly moving nutrients downstream (Newbold et al. 1981). One complete turn of the spiral represents a solute in the water column being assimilated to an organic form in the benthos before returning back to the water column (Figure 1.1). The total length of a spiral can be described as having two parts: turnover length (S_b), the distance a solute travels in the benthos until mineralization, and uptake length (S_w), the distance a solute travels in the water column until assimilation (Webster and Valett 2006). Total spiral length is dominated by S_w (Newbold et al. 1981) due to the limited mobility of stream biota compared with the velocity of stream flow. S_w is affected by abiotic factors such as stream discharge, velocity, sediment texture, and nutrient concentration. For example, increases in discharge and velocity contribute to longer S_w because stream surface area to volume ratio decreases at higher flow, reducing contact of the benthos with dissolved solutes. Biotic factors such as microbial and algal productivity can also affect S_w due to variable competition for nutrients. In boreal forest headwater streams, low light availability due to canopy cover and cold stream water temperature may limit algal and microbial productivity. This could contribute to longer S_w in boreal streams than in other ecosystems with greater in-stream productivity and nutrient demand (Tank et al. 2008).

1.3 Hydrology affects nutrient flux to streams

Hydrologic flowpaths affect the chemical composition of dissolved organic matter (DOM) that reaches streams (Balcarczyk et al. 2009) and total flux of dissolved organic carbon (DOC) and inorganic nutrients (Petrone et al. 2006). DOM is sourced from in-stream algal productivity and from the surrounding catchment. Inorganic nutrients are contributed to streams

from weathering of mineral soils and also from leaching and microbial mineralization of DOM. For example, leaf litter can provide a significant addition of soluble reactive phosphorus to streams (Schreeg et al. 2013) through leaching via shallow flowpaths. Ground water contains less DOM than surface water (O'Donnell et al. 2012) in large part due to adsorption of DOM to mineral soil (Kawahigashi et al. 2004) and contributes a greater proportion to base flow than shallow surface flow in streams draining watersheds lacking permafrost (Jones and Rinehart 2010). In the Caribou-Poker Creeks Research Watershed (CPCRW) in the boreal forest of interior Alaska, base flow in a low permafrost catchment contributes ~80% of stream discharge compared with 44% in a high permafrost catchment (Jones and Rinehart 2010). In deep flowpaths, the hydrophobic portions of DOM preferentially sorb to mineral soil, resulting in a decrease in DOM concentration and a fractionation of DOM such that the hydrophilic, labile components are more readily delivered to stream water (Kawahigashi et al. 2004). In contrast, streams in catchments with high permafrost extent and a shallow active layer have a greater concentration of DOM during baseflow and storms (Petrone et al. 2006) and proportionally more DOM that is recalcitrant (Balcarczyk et al. 2009).

1.4 Ecosystem stoichiometry

The ratios of biologically important solutes such as nitrogen (N), phosphorus (P), and carbon (C) can affect microbial growth (Frost et al. 2002, Sterner and Elser 2002). The concept of ecosystem stoichiometry has its origins in Redfield (1958), who proposed that the N:P ratios in ocean water were biogeochemically linked with the N:P ratios in phytoplankton.

Stoichiometry in freshwater tends to vary from what Redfield found in the open ocean (Hassett et al. 1997) due to differences in biotic community structure and nutrient availability. For

example, streams dominated by heterotrophy are more homeostatic than autotrophic streams in regards to nutrient assimilation (Schade et al. 2011). Heterotrophs assimilate both organic and inorganic nutrients (Stelzer et al. 2003) in relatively fixed ratios and thus are limited in their capacity to incorporate nutrients beyond their immediate needs (Sternner and Elser 2002). Experimental N and P enrichment in autotrophic and heterotrophic streams has shown that streams dominated by autotrophy have a greater flexibility in N and P uptake (Schade et al. 2011). Following predictions from ecosystem stoichiometry, heterotrophic uptake of DOC, N, and P should be maximized at C:N and C:P closest to microbial biomass, which tends to have lower carbon to nutrient ratios when compared with autotrophic organisms (Sternner and Elser 2002).

Photosynthetic rates are low in high latitude streams, making allochthonous carbon inputs critical to sustaining microbial respiration and growth (Peterson et al. 1986), and low available N and/or P may constrain stream productivity. In the Kuparuk River in arctic Alaska, fertilization with phosphorus increased stream productivity by relieving P limitation (Peterson et al. 1985). In contrast to the Kuparuk River with its open canopy, forested streams in the CPRW in interior Alaska tend to have low light availability and are dominated by heterotrophy (Betts and Jones 2009), which may make these streams limited by organic carbon. Whole-stream experiments have found that stream microbial uptake responds to the addition of labile DOC; for example, uptake of inorganic nitrogen increased with the addition of acetate (a labile form of DOC; Bernhardt and Likens 2002). As a result, DOC bioavailability could constrain uptake of inorganic nutrients in streams with low autochthonous production and high heterotrophic organic carbon demand.

1.5 DOM bioavailability

DOM is a complex and variable assortment of organic molecules (Amon and Meon 2004, Seitzinger et al. 2005) and lability, how readily DOM is degraded, is related to its molecular structure. Black spruce and other conifers contain more resins and phenolic compounds than deciduous plants, resulting in coniferous forest contributing more recalcitrant DOM than deciduous vegetation (Moore et al. 2006). In the CPRW, the proportion of biodegradable DOC in low-permafrost catchment streams is greater than in streams of high permafrost catchments (Balcarczyk et al. 2009). Likewise, in streams of interior Alaska, DOM from groundwater shows characteristics of a labile carbon source as determined by fluorescence properties and chemical fractionation of the DOM (O'Donnell et al. 2012). Water residence time in catchment soils can also affect DOM lability, as spring water in the CPRW shows differences in DOM composition with varying groundwater residence time (White et al. 2008). Microbial preprocessing of DOM could lead to relatively less labile DOC in catchments with a long groundwater residence time. Nutrients have variable effects on DOM lability (Balcarczyk et al. 2009), potentially enhancing biodegradability of recently leached, relatively unprocessed DOM (Holmes et al. 2008).

1.6 Predicted changes in stream chemistry

High latitude streams play an important role in the global carbon cycle by transporting and transforming organic carbon. Loss of permafrost may change carbon and nutrient uptake in boreal forest streams due to increased delivery of inorganic nutrients and bioavailability of DOM (Fig. 1.2). In Figure 1.2, panel A depicts a catchment underlain with permafrost, where black spruce and moss vegetation contribute to a cold, poorly drained soil that is high in recalcitrant organic matter. As a result, much of the DOM received by the stream is exported downstream

unchanged and uptake of nutrients is relatively low. Panel B illustrates how a loss of permafrost could lead to a greater proportion of bioavailable DOM due to changing catchment vegetation and deeper catchment flowpaths, as well as increased input of inorganic nutrients from soil weathering and microbial mineralization.

Recent alteration of nutrient flux in high latitude streams is evidenced by increases in stream nitrate concentration in the Kuparuk River in arctic Alaska (McClelland et al. 2007), net nitrate loss from boreal forest watersheds in interior Alaska (Jones et al. 2005), and a decrease in DOC concentration in the Yukon River (Striegl et al. 2005). The fraction of highly aromatic DOM is predicted to decrease in the Yukon River as deeper ground water contributes more to stream flow (O'Donnell et al. 2012), suggesting that permafrost thaw may lead to overall declines in refractory DOM in other boreal rivers and streams. These observations provided the motivation for my study to examine the coupling between organic carbon and inorganic nutrients in boreal forest streams. I chose nine streams with variable ambient chemistry to measure nutrient uptake using pulsed additions of DOM, N, and P, and I aimed to test the following research questions: How does variable nutrient stoichiometry affect uptake of DOC, N, and P? How does the variability in DOM chemistry affect nutrient uptake? I compared several metrics of nutrient spiraling (Stream Solute Workshop 1990), calculated using the tracer additions for spiraling curve characterization (TASCC) method (Covino et al. 2010), to measure uptake of DOC, N, and P in boreal forest headwater streams.

1.7 Figures

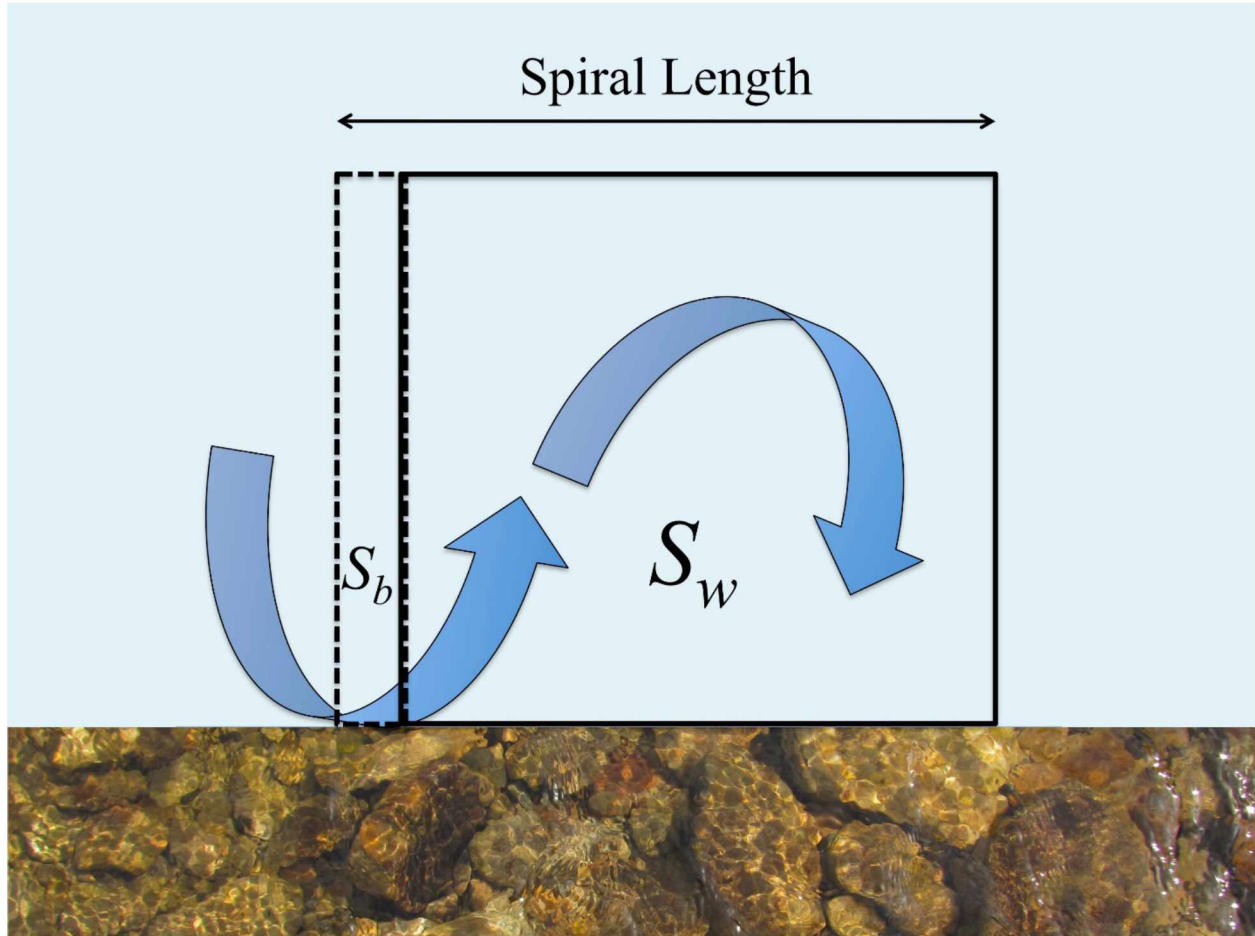


Figure 1.1. Conceptualization of a stream nutrient spiral. A nutrient spiral represents solutes in the water column being assimilated into the benthos, and eventually returning to the water column through mineralization. Spiral length is composed of two parts: turnover length (S_b), the distance a solute travels in the benthos before mineralization, and uptake length (S_w), the distance a solute travels in the water column before assimilation. S_w comprises the majority of total spiral length.

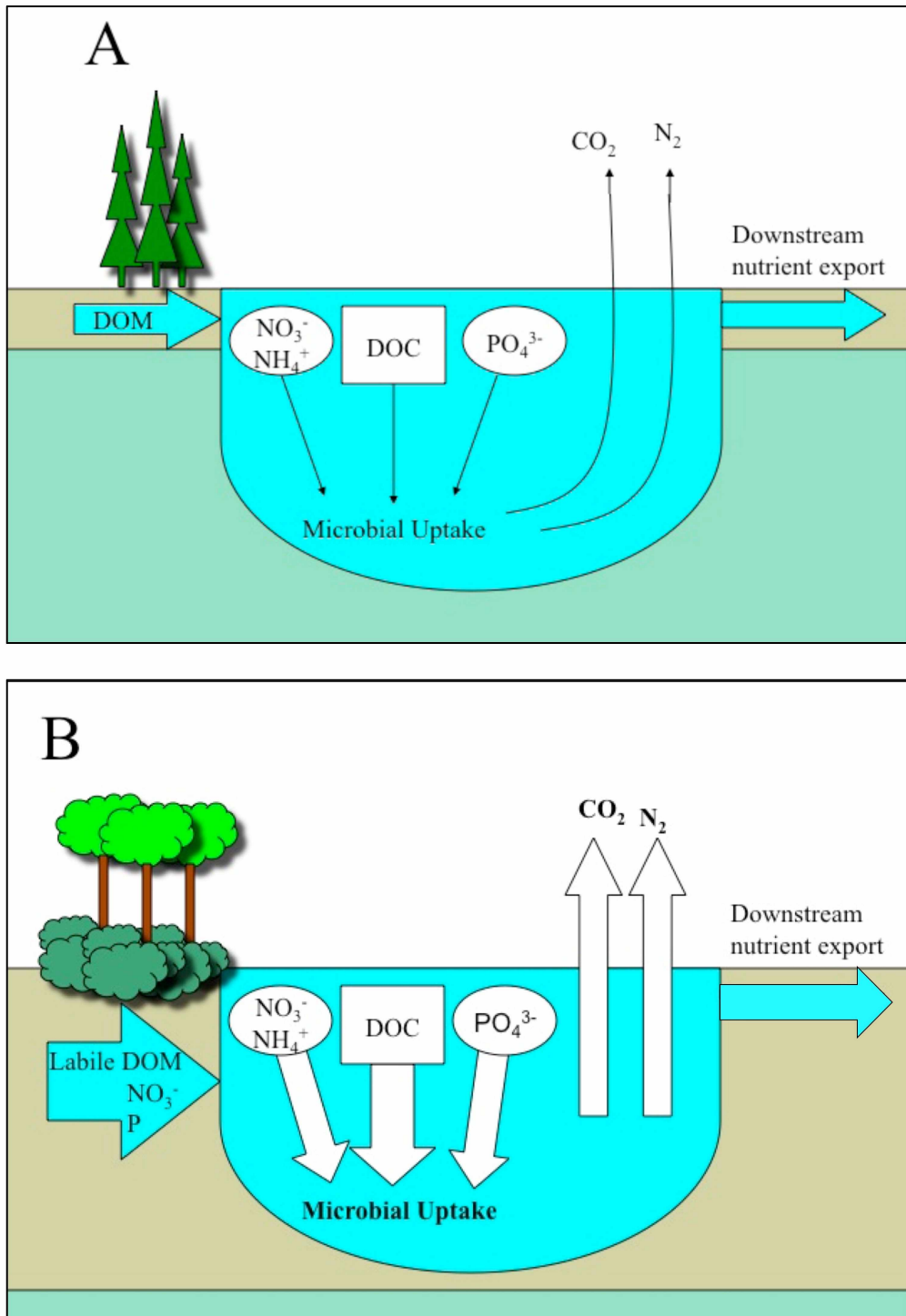


Figure 1.2. Diagram of the predicted effects of permafrost on stream chemistry. Panel A depicts a high permafrost stream and panel B depicts the potential consequences of permafrost loss for stream chemistry and nutrient uptake. Arrow size indicates relative magnitude of nutrient flux.

1.8 Literature Cited

- Amon, R. M. W. and B. Meon. 2004. The biogeochemistry of dissolved organic matter and nutrients in two large Arctic estuaries and potential implications for our understanding of the Arctic Ocean system. *Marine Chemistry* **92**:311-330.
- Balcarczyk, K. L., J. B. Jones, R. Jaffé, and N. Maie. 2009. Stream dissolved organic matter bioavailability and composition in watersheds underlain with discontinuous permafrost. *Biogeochemistry* **94**:255-270.
- Bengtsson, G. and N. Törneman. 2004. Dissolved organic carbon dynamics in the peat-streamwater interface. *Biogeochemistry* **70**:93-116.
- Bernhardt, E. S. and G. E. Likens. 2002. Dissolved organic carbon enrichment alters nitrogen dynamics in a forest stream. *Ecology* **83**:1089-1700.
- Betts, E. F. and J. B. Jones. 2009. Impact of wildfire on stream nutrient chemistry and ecosystem metabolism in boreal forest catchments of interior Alaska. *Arctic, Antarctic, and Alpine Research* **41**:407-417.
- Covino, T. P., B. L. McGlynn, and R. A. McNamara. 2010. Tracer Additions for Spiraling Curve Characterization (TASCC): Quantifying stream nutrient uptake kinetics from ambient to saturation. *Limnology and Oceanography: Methods* **8**:484-498.
- Fisher, S. G. and G. E. Likens. 1973. Energy flow in Bear Brook, New Hampshire: An integrative approach to stream ecosystem metabolism. *Ecological Monographs* **43**:421-439.
- Frost, P. C., R. S. Stelzer, G. A. Lamberti, and J. J. Elser. 2002. Ecological stoichiometry of trophic interactions in the benthos: Understanding the role of C:N:P ratios in lentic and lotic habitats. *Journal of the North American Benthological Society* **21**:515-528.

- Hassett, R. P., B. Cardinale, L. B. Stabler, and J. J. Elser. 1997. Ecological stoichiometry of N and P in pelagic ecosystems: Comparison of lakes and oceans with emphasis on the zooplankton-phytoplankton interaction. *Limnology and Oceanography* **42**:648-662.
- Holmes, R. M., J. W. McClelland, P. A. Raymond, B. B. Frazer, B. J. Peterson, and M. Stieglitz. 2008. Lability of DOC transported by Alaskan rivers to the Arctic Ocean. *Geophysical Research Letters* **35**:L03402.
- Jones, J. B., K. C. Petrone, J. C. Finlay, L. D. Hinzman, and W. R. Bolton. 2005. Nitrogen loss from watersheds of interior Alaska underlain with discontinuous permafrost. *Geophysical Research Letters* **32**:L02401.
- Jones, J. B. and A. J. Rinehart. 2010. The long-term response of stream flow to climatic warming in headwater streams of interior Alaska. *Canadian Journal of Forest Research* **40**:1210-1218.
- Jorgensen, M. T., V. Romanovsky, J. Harden, Y. Shur, J. A. O'Donnell, E. A. Schuur, M. Kanevskiy, and S. Marchenko. 2010. Resilience and vulnerability of permafrost to climate change. *Canadian Journal of Forestry Research* **40**:1219-1236.
- Kawahigashi, M., K. Kaiser, K. Kalbitz, A. Rodionov, and G. Guggenberger. 2004. Dissolved organic matter in small streams along a gradient from discontinuous to continuous permafrost. *Global Change Biology* **10**:1576-1586.
- MacLean, R., M. W. Oswood, J. G. I. Irons, and W. H. McDowell. 1999. The effect of permafrost on stream biogeochemistry: A case study of two streams in the Alaskan (U.S.A.) taiga. *Biogeochemistry* **47**:239-267.

- McClelland, J. W., M. Stieglitz, F. Pan, R. M. Holmes, and B. J. Peterson. 2007. Recent changes in nitrate and dissolved organic carbon export from the upper Kuparuk River, North Slope, Alaska. *Journal of Geophysical Research* **112**:G04560.
- Moore, T. R., J. A. Trofymow, C. E. Prescott, J. Fyles, and B. D. Titus. 2006. Patterns of carbon, nitrogen and phosphorus dynamics in decomposing foliar litter in Canadian forests. *Ecosystems* **9**:46-62.
- Newbold, J. D., J. W. Elwood, R. V. O'Neill, and W. Van Winkle. 1981. Measuring nutrient spiralling in streams. *Canadian Journal of Fisheries and Aquatic Sciences* **38**:860-863.
- O'Donnell, J. A., G. R. Aiken, M. A. Walvoord, and K. D. Butler. 2012. Dissolved organic matter composition of winter flow in the Yukon River basin: Implications of permafrost thaw and increased groundwater discharge. *Global Biogeochemical Cycles* **26**:GB0E06.
- Permafrost Subcommittee. 1988. Glossary of permafrost and related ground-ice terms. Page 156 *in* National Research Council of Canada, Ottawa.
- Peterson, B. J., J. E. Hobbie, A. Hershey, M. Lock, T. Ford, R. Vestal, M. Hullar, R. Ventullo, and G. Volk. 1985. Transformation of a tundra stream from heterotrophy to autotrophy by addition of phosphorus. *Science* **229**:1382-1386.
- Peterson, B. J., J. E. Hobbie, and T. L. Corliss. 1986. Carbon flow in a tundra stream ecosystem. *Canadian Journal of Fisheries and Aquatic Sciences* **43**:1259-1270.
- Petrone, K. C., J. B. Jones, L. D. Hinzman, and R. D. Boone. 2006. Seasonal export of carbon, nitrogen, and major solutes from Alaskan catchments with discontinuous permafrost. *Journal of Geophysical Research* **111**:G02020.
- Redfield, A. C. 1958. The biological control of chemical factors in the environment. *American Scientist* **46**:205-221.

- Schade, J. D., K. MacNeill, S. A. Thomas, F. C. McNeely, J. R. Welter, J. Hood, M. Goodrich, M. E. Power, and J. C. Finlay. 2011. The stoichiometry of nitrogen and phosphorus spiralling in heterotrophic and autotrophic streams. *Freshwater Biology* **56**:424-436.
- Schreeg, L. A., M. C. Mack, and B. L. Turner. 2013. Nutrient-specific solubility patterns of leaf litter across 41 lowland tropical woody species. *Ecology* **94**:94-105.
- Seitzinger, S. P., H. Hartnett, R. Lauck, M. Mazurek, T. Minegishi, G. Spyres, and R. Styles. 2005. Molecular-level chemical characterization and bioavailability of dissolved organic matter in stream water using electrospray-ionization mass spectrometry. *Limnology and Oceanography* **50**:1-12.
- Stelzer, R. S., J. Heffernan, and G. E. Likens. 2003. The influence of dissolved nutrients and particulate organic matter quality on microbial respiration and biomass in a forest stream. *Freshwater Biology* **48**:1925-1937.
- Sterner, R. W. and J. J. Elser. 2002. *Ecological stoichiometry: The biology of elements from molecules to the biosphere*. Princeton University Press, Princeton, NJ.
- Striegl, R. G., G. R. Aiken, M. M. Dornblaser, P. A. Raymond, and K. P. Wickland. 2005. A decrease in discharge-normalized DOC export by the Yukon River during summer through autumn. *Geophysical Research Letters* **32**:L21413.
- Stream Solute Workshop. 1990. Concepts and methods for assessing solute dynamics in stream ecosystems. *Journal of the North American Benthological Society* **9**:95-119.
- Tank, J. L., E. J. Rosi-Marshall, M. A. Baker, and R. O. Hall. 2008. Are rivers just big streams? A pulse method to quantify nitrogen demand in a large river. *Ecology* **89**:2935-2945.

- Tarnocai, C., J. G. Canadell, E. A. G. Schuur, P. Kuhry, G. Mazhitova, and S. Zimov. 2009. Soil organic carbon pools in the northern circumpolar permafrost region. *Global Biogeochemical Cycles* **23**:GB2023.
- Viereck, L. A., C. T. Dyrness, K. Van Cleve, and J. M. Foote. 1983. Vegetation, soils, and forest productivity in selected forest types in interior Alaska. *Canadian Journal of Forestry Research* **13**:703-720.
- Webster, J. R. and H. M. Valett. 2006. Solute Dynamics. Pages in 169-185 *in* F. R. Hauer and G. A. Lamberti, editors. *Methods in Stream Ecology*, Second Edition. Academic Press, San Diego, USA.
- White, D., V. Autier, K. Yoshikawa, J. Jones, S. Seelen. 2008. Using DOC to better understand local hydrology in a subarctic watershed. *Cold Regions Science and Technology* **51**:68-75.
- Zhang, T., R. G. Barry, K. Knowles, J. A. Heginbottom, and J. Brown. 1999. Statistics and characteristics of permafrost and ground-ice distribution in the Northern Hemisphere. *Polar Geography* **23**:132-154.

Chapter 2: Coupling the effects of dissolved organic matter and nutrient stoichiometry with nutrient uptake in boreal forest headwater streams¹

2.1 Abstract

Discontinuous permafrost affects the hydrology of boreal forest streams by restricting flow path depth where permafrost is present. Stream water chemistry, such as flux of inorganic nutrients and dissolved organic matter (DOM), is subsequently affected by permafrost distribution. Headwater streams in the boreal forest are dependent on allochthonous inputs of energy and nutrients, and as a result are dominated by heterotrophic processes. A warming climate may change the distribution of permafrost in high latitude ecosystems, with consequences for nutrient availability. Herein, we investigated how nutrient stoichiometry interacts with the availability of labile carbon to control nutrient uptake. We hypothesized that 1) the carbon, nitrogen, and phosphorus (C:N:P) ratio in DOM affects nutrient uptake due to stoichiometric constraints on autotrophic and heterotrophic nutrient assimilation, and 2) labile DOM affects nutrient uptake by increasing heterotrophic production. We tested these hypotheses using a series of instantaneous nutrient additions with a factorial design manipulating both C:N:P ratios and DOM source (acetate or birch leaf leachate) in nine headwater streams in interior Alaska. We added N and P (as NH_4^+ and PO_4^{3-}) alone, simultaneously, and in combination as DOM. Uptake velocities (V_{f-amb}) for C, N, and P were within the upper range of literature values from other ecosystems, ranging from 4.1 – 67.2 mm/min for N, 4.0 – 25.0 mm/min for P, and 4.2 – 34.5 mm/min for acetate. V_{f-amb} was in part explained by ambient stream chemistry, with N V_{f-amb} weakly positively correlated with ambient P concentration, while uptake velocity for SRP and

¹ Fjare, D., J. B. Jones, and T. K. Harms. Coupling the effects of dissolved organic matter and nutrient stoichiometry with nutrient uptake in boreal forest headwater streams, prepared for submission to *Ecology*.

acetate was weakly negatively correlated with ambient inorganic N and ambient dissolved organic carbon (DOC), respectively. In addressing our nutrient stoichiometry hypothesis, we found uptake efficiency (U_E) was similar for N and P added alone, in co-additions, and with DOM. For our labile DOM hypothesis, acetate and birch-derived DOM had similar effects on N and P U_E during in-stream additions. During laboratory incubations both carbon sources were very labile with $\geq 70\%$ of acetate and birch-DOM mineralized over 30 days. Overall, our results were inconclusive as to whether DOM stoichiometry or source affected uptake, but the addition of inorganic nitrogen increased DOC loss from birch DOM. High demand for nutrients in boreal forest headwater streams suggests that uptake could increase concurrently with greater inorganic nutrient flux following a loss in permafrost extent, and that response in stream nutrient uptake is relatively flexible to changes in DOM source and nutrient stoichiometry.

2.2 Introduction

Headwater streams are important sites of nutrient transformation and uptake (Peterson et al. 2001, Ensign and Doyle 2006) because they are often the first interface between the aquatic and terrestrial ecosystem as solutes travel from catchment soil downstream into rivers or larger bodies of water (MacDonald and Coe 2006). Relative to rivers, headwater streams are more influenced by their catchments and can be dependent upon allochthonous inputs of energy and nutrients (Gomi et al. 2002). A diverse community of microorganisms drives nutrient cycling in headwater streams, with heterotrophic and autotrophic organisms having different nutrient and energy requirements for growth and metabolism. Heterotrophic microbes are dependent on organic carbon for energy, whereas autotrophs need adequate light for photosynthesis. Both groups of microorganisms compete to assimilate inorganic nutrients, the most important of

which are nitrogen and phosphorus. Nutrients may limit stream productivity if either inorganic nitrogen or phosphorus is present at low concentration (Peterson et al. 1985, Goldman et al. 1990). Organic carbon in streams has variable bioavailability (White et al. 2008, Balcarczyk et al. 2009, Wickland et al. 2012), which is affected by differing carbon chemistry (Wickland et al. 2007) and prior microbial processing (Kaplan and Bott 1983). The close linkage between headwater streams and their catchments leaves first-order streams particularly sensitive to changes in nutrient and organic matter inputs.

Ecological stoichiometry predicts that the biogeochemical cycling of nutrients is directly related to the ratios of those elements in organisms (Reiners 1986, Sterner and Elser 2002), with feedbacks between biotic demand, nutrient inputs, and nutrient availability (Redfield 1958, Elser and Urabe 1999). Within streams, element stoichiometry can affect the balance of autotrophic and heterotrophic production, with consequences for nutrient cycling. Heterotrophs, such as bacteria, are dependent upon organic sources of carbon for growth and metabolism and maintain stricter homeostasis in their body carbon, nitrogen, and phosphorus ratio (C:N:P) than autotrophic algae, which fix their own carbon and store extra nutrients in specialized organelles. As a result, autotrophic stream communities display more flexibility in uptake of nutrients than do heterotrophic stream communities (Schade et al. 2011).

Forested headwater streams have low primary productivity and are subsidized by allochthonous inputs, with as much as 99% of the energy input derived from catchment vegetation and subsurface flow (Fisher and Likens 1973). At high latitudes, where low light incidence limits aquatic primary productivity, dissolved organic matter (DOM) contributes to as much as 90% of the organic carbon pool in streams (Peterson et al. 1986). Consequently, headwater streams can be predominantly heterotrophic ecosystems that use DOM as an energy

source. DOM is leached from leaves and soil (Kaplan and Newbold 1993) and inputs of DOM to streams are linked with catchment flowpaths (Mulholland et al. 1990a), where shallow flowpaths contribute more recently leached DOM. DOM affects nutrient ratios in stream water and nutrient demand by serving as both a carbon source and potentially as a source of N and P (Marschner and Kalbitz 2003, Mineau et al. 2013). Due to the importance of allochthonous DOM to microbial productivity in forested headwater streams, inorganic nutrient uptake should be linked with DOM lability.

In the boreal forest of interior Alaska, discontinuous permafrost shapes catchment hydrology by restricting flow path depth where permafrost is present, affecting the fluxes of DOM and solutes delivered to streams (MacLean et al. 1999, Petrone et al. 2006). Changing sources of water to streams may also alter the bioavailability of DOM, with deeper flowpaths potentially contributing proportionally more biologically available, or labile, DOM to streams (O'Donnell et al. 2012). Increasing temperature in the Northern Hemisphere has led to warming of permafrost (Romanovsky et al. 2010), with discontinuous permafrost especially vulnerable to thaw because the temperature is just below freezing (Jorgensen et al. 2010). Discharge-normalized dissolved organic carbon (DOC) concentration has declined in Alaskan rivers (Striegl et al. 2005, O'Donnell et al. 2012) and nitrate concentration has increased (Jones et al. 2005, Petrone et al. 2006, McClelland et al. 2007), potentially linked to permafrost thaw. Decline in DOC concentration may reduce heterotrophic assimilation of N and P due to energetic constraints on uptake, resulting in streams being less retentive of inorganic nutrients.

The goal of our study was to determine how nutrient stoichiometry and carbon bioavailability interact to affect nutrient uptake in boreal forest streams. We hypothesized that inorganic N:P ratios and the C:N:P ratios in DOM affect uptake due to stoichiometric constraints

on autotrophic and heterotrophic nutrient uptake. Autotrophic uptake is constrained by available inorganic nutrients, whereas heterotrophic uptake is also constrained by organic carbon availability and is less flexible in the ratio of N:P assimilated. In addition, we hypothesized that labile organic carbon from DOM affects nutrient uptake by increasing heterotrophic production. To test our hypotheses, we added N and P alone and in combination in nine boreal forest headwater streams. Using a factorial design we manipulated DOM source using acetate and birch litter leachate, and for each DOM source we contrasted C:N:P at two different ratios. We predicted that the co-addition of N and P would increase uptake by alleviating stoichiometric limitation of autotrophs, and low N:P would alleviate stoichiometric limitation of heterotrophs. Likewise, the addition of C would further increase heterotrophic nutrient uptake by providing an organic carbon source, and lower C:Nutrient ratios were expected to facilitate increased uptake because the DOM source more closely matched the stoichiometry of microbial consumers.

2.3 Methods

2.3.1 Study sites

Our research was conducted in boreal forest headwater streams in interior Alaska, approximately 50 km NE of Fairbanks, Alaska (65°10' N, 147°30' W). The regional climate is continental, characterized by large fluctuations in annual temperature (average of 16.4°C in July and -24.9°C in January) and low annual precipitation (ca. 270 mm). Nine headwater streams with varying ambient chemistry were selected, with five located in the Caribou-Poker Creeks Research Watershed (CPCRW) and four located along the Steese Highway (Fig. 2.1, Fig. A.1-A.7). Catchment area ranged from 5.2 to 47.6 km² (Table A.1).

Vegetation in the boreal forest is related to permafrost distribution and aspect (Viereck et al. 1983), with warmer south-facing slopes populated by deciduous hardwoods (*Betula neolaskana*, *Populus tremuloides*), and the north-facing slopes and valley bottoms dominated by black spruce (*Picea mariana*), mosses (*Sphagnum spp.*, *Hylocomium spp.*), and lichens. The dominant vegetation in riparian areas is shrubs (*Vaccinium spp.*), willow (*Salix spp.*), and alder (*Alnus tenuifolia*). Sub-catchments of the CPRW vary in areal extent of permafrost with coverage ranging from 4% to 53% (Table A.1). Permafrost extent has not been estimated for the other catchments. The study area has a history of wildfire with an average return interval of 43 years (Yarie 1981), and many of the catchments in this study were affected by a wildfire in 2004. In the CPRW, a recently burned catchment had increased stream nitrate concentration and decreased DOC and dissolved organic nitrogen (DON) concentration relative to unburned catchments (Betts and Jones 2009).

2.3.2 Experimental design

Nutrient additions were conducted between June 30 and August 2, 2013. A total of eight different nutrient mixtures were added per stream following a factorial design manipulating C:N:P ratios (Table 2.1), DOM source (Table 2.1), and inorganic N:P ratios (Table 2.2). We tested our first hypothesis, that nutrient ratios would affect uptake, by setting up a contrast between additions of inorganic nutrients with ratios of 6N:1P (below the Redfield ratio of 16N:1P) and 35N:1P (above the Redfield ratio), and acetate-DOM additions with ratios of 383C:3N:1P (approximating the high C:N ratios in the birch leachate) and 89C:8N:1P (near the Redfield ratio of 106C:16N:1P). To address our second hypothesis, we contrasted carbon source using DOM derived from either acetate or birch. Acetate is a labile form of DOC that is used by

aquatic microorganisms (Hall and Meyer 1998) and the birch leachate is a relatively more complex source of DOC (Wickland et al. 2007).

2.3.3. Nutrient addition preparation

The birch leachate was made from the leaves of young *Betula neoalaskana* collected on June 22, 2013 from the CPCRW. In the lab, leaves were dried in paper bags in an oven at 60°C for at least 48 hours. Dried leaves were then ground in a food processor until fine. Approximately 5 kg of leaves were mixed with ultrapure water and leached for 24 hours in a cold room. About 0.07 mgC/mg dried leaf litter was leached into solution, resulting in a leachate concentration of 14 gC/L. The leachate was filtered through 6.4 thread/cm mesh into a carboy, from which the DOM was transferred to low density polyethylene containers and frozen until the day it was used for the nutrient additions.

We varied N and P concentration by adding NH_4Cl and H_2KPO_4 , respectively, at the amounts in Table 2.2. DOM source was manipulated by adding either acetate ($\text{C}_2\text{H}_3\text{NaO}_2$ or glacial acetic acid, diluted and neutralized with NaHCO_3) or the birch leachate (Table 2.1). Salts were mixed into solution with ultrapure water. Sodium chloride was used as the conservative tracer and raised specific conductivity at least 15 $\mu\text{S}/\text{cm}$ above background and chloride at least 0.5 mgCl/L above background. The target concentration of carbon in the DOM additions was 12 gC/L. For the inorganic additions, the mass of N was kept constant and N:P ratios were manipulated by varying the mass of P. A small volume from each injectate was frozen for later analysis.

2.3.4 Nutrient additions

Our goal was to conduct the nutrient additions in rapid succession to avoid temporal changes in light, temperature, and discharge. Reach lengths varied from 80 to 172 m and were based on an arrival time of about 6 minutes for the injection, with the entire nutrient addition passing the sampling station within 45 minutes. We detected the arrival of the addition using a sonde (YSI ProfessionalPlus Series) logging specific conductivity at one-second intervals. To establish the timing of sampling across the breakthrough curve, we used a slug of sodium chloride at each stream before beginning the nutrient additions. The resulting breakthrough curve was divided into 22 sampling points intended to equally sample the rising limb, peak, and falling limb of each injection. Before adding nutrients, a background water sample was collected. Time was allowed in between each nutrient addition for the stream to return to ambient conductivity. We collected water samples into acid-washed 60 mL polyethylene bottles and stored them in a cooler until returning to the lab. In the lab, water samples were filtered through a 0.7 μm pore size Whatman glass-fiber filter within 24 hours. Samples that were not analyzed immediately after filtering were poured into acid-washed 20 mL scintillation vials and frozen.

Stream width was calculated as the average of at least ten measurements along the experimental reach. Each set of eight nutrient additions occurred within the same stream reach on the same day, and the order of additions was random for each stream. Discharge (Q , in L/s) was determined using chloride dilution gauging for each nutrient addition, calculated as

$$Q = \frac{M}{\int_0^t (C_i - C_0) dt} \quad (1)$$

where M is the conductivity of the chloride injectate (in $\mu\text{S}/\text{cm}$), C_i is the measured stream conductivity at one second intervals, and C_0 is the background stream conductivity. Water flow

velocity was calculated as the total reach length divided by the travel time for chloride from the peak of the breakthrough curve.

2.3.5 Laboratory incubations for carbon lability

We set up laboratory incubations of our solutions of birch and acetate-DOM to determine relative lability. The design of our incubation followed that of the whole-stream experimental additions, manipulating both carbon source and nutrient ratios using combinations of organic and inorganic nutrients (Table 2.3). We adapted our incubation experimental protocol from Holmes et al. (2008), measuring DOC lost from the incubation over time as representative of the labile DOC pool. In our experiment, we quantified DOC loss over 30 days, with a sub-sampling after six days to measure rapid DOC loss.

We made four nutrient treatments by diluting birch and acetate solutions to a target concentration of 12 mgC/L. The starting DOC concentration in the incubations was intended to be great enough to reliably detect DOC loss, but was higher than the ambient DOC concentration in the study streams (mean of 2.3 mgC/L). Each nutrient treatment had six replicates, and each replicate contained 40 mL of DOM solution and 2 mL of unfiltered stream water as the inoculum. Solutions were incubated in lidded glass jars in the dark at room temperature. Initial samples were taken immediately after completing the incubation set-up. To take samples, 14 mL of water was drawn from each jar using a macropipette and filtered through a 0.2 μ m Whatman nuclepore track-etch membrane filters using a glass filter tower and vacuum. Filtered samples were transferred to ashed glass scintillation vials, acidified with 100 μ L of 5N HCl, and refrigerated until analysis.

2.3.6 Chemical analyses

DOC (limit of quantification 0.10 mgC/L) and total dissolved nitrogen (TDN, limit of quantification 20 µgN/L) were measured on a Shimadzu TOC-5000 connected to an Antek 7050 nitric oxide chemoluminescent detector. Soluble reactive phosphorus (SRP, limit of quantification 0.5 µgP/L) was measured on a Shimadzu UVmini 1240 spectrophotometer with a 5 cm cell using the molybdate blue method. Anions (Cl^- and NO_3^- , limit of quantification 0.03 mgCl/L and 1.3 µgN/L) and cations (NH_4^+ , limit of quantification 3 µgN/L) were quantified using a Dionex DX-320 Ion Chromatograph. Chloride and ammonium for the TASCC additions were measured on a Smartchem 170 using the mercuric thiocyanate (limit of quantification 0.5 mgCl/L) and the phenol hypochlorite (limit of quantification 4 µgN/L) methods, respectively. Specific ultra-violet absorption (SUVA), a measure of the relative complexity of DOC, was measured on a Shimadzu UVmini 1240 spectrophotometer at a wavelength of 254 nm.

2.3.7 Uptake calculations

We calculated nutrient uptake metrics using the tracer additions for spiraling curve characterization (TASCC) method (Covino et al. 2010). TASCC measures in-stream nutrient uptake by quantifying the loss of reactive nutrient along a reach relative to a conservative tracer during a pulsed nutrient addition. The advantage of TASCC compared with previous methods of measuring nutrient uptake is that TASCC additions are relatively short (< 1 hour to complete), inexpensive, and yield a range of nutrient concentrations at a single downstream sampling point. One injection can provide estimates of several uptake metrics for a stream reach, such as uptake length, areal uptake, and uptake velocity.

The exponential decline in nutrient concentration with distance downstream from the addition point was calculated as

$$k_w = \frac{\ln[N:CI]_{stream} - \ln[N:CI]_{injectate}}{D} \quad (2)$$

where k_w is the decline in the ratio of reactive to conservative solute ($[N:CI]$) in the breakthrough curve and injectate over reach length (D , in m). Uptake length (S_w , in m), the average distance a molecule travels before being immobilized from the water column, was calculated as

$$S_w = \frac{-1}{k_w} \quad (3)$$

S_w at ambient nutrient concentration (S_{w-amb}) was calculated as the intercept of S_w plotted against the geometric mean of total observed and expected nutrient concentration (Payn et al. 2005), where expected nutrient concentration is based on the recovery of conservative tracer. For DOC, we estimated S_{w-amb} from the background-corrected DOC because we did not measure the ambient concentration of acetate or birch DOM. As a result, uptake of added labile DOC likely overestimates demand for in-stream DOC. If the slope of S_w versus geometric mean nutrient concentration was not significantly different from zero at the $\alpha = 0.05$ level we calculated S_{w-amb} as the weighted average for S_w from that addition.

Areal uptake (U , in $\mu\text{g m}^{-2}\text{min}^{-1}$) describes rates of biotic uptake, and was calculated as

$$U = \frac{Q \times [N]}{S_w \times w} \quad (4)$$

where $[N]$ is the concentration of the nutrient of interest and w is wetted stream width. Microbial uptake in streams is predicted to follow a Michaelis-Menten relationship with U saturating at higher nutrient concentrations (Payn et al. 2005), but linear relationships have also been

observed, presumably when uptake capacity is not saturated (Earl et al. 2006, O'Brien and Dodds 2010).

Uptake length (S_w) and areal uptake (U) are both affected by stream discharge, velocity, and nutrient concentration. Uptake velocity (V_f , in mm min^{-1}) standardizes U and S_w to allow comparison of relative nutrient demand among different streams (Webster and Valett 2006). V_f was calculated as

$$V_f = \frac{U}{[N]} \quad (5)$$

and V_f at ambient nutrient concentration (V_{f-amb}) was calculated from S_{w-amb} by

$$V_{f-amb} = \frac{Q}{S_{w-amb} \times w} \quad (6)$$

Samples in the breakthrough curve were excluded from the dataset when solute concentration was within two standard deviations of the detection limit. Additions for which the correlation between reactive and conservative solutes across the breakthrough curve had $R^2 < 0.8$ were likewise omitted from the final analysis. Additions were also removed if S_{w-amb} was negative, which could result from inaccurately measured solute ratios of the injectate or breakthrough curve samples. The increase in stream NH_4^+ concentration during the birch addition was below detection limits, so we were unable to measure NH_4^+ uptake for that treatment.

2.3.8 Statistical analyses

For in-stream nutrient additions we used linear regression to estimate S_{w-amb} . We used AIC to select between a linear or Michaelis-Menten model to estimate the slope of U versus geometric mean nutrient concentration. This slope (hereafter referred to as U_E) is a measure of uptake efficiency, the magnitude of which is related to how rapidly U increases relative to added nutrient concentration. U_E was used instead of V_{f-amb} to test for a response in nutrient uptake to changing stoichiometry and DOM chemistry, because estimates of nutrient uptake for ambient conditions assume no effect of nutrient manipulation. V_{f-amb} of NH_4^+ was log-transformed and compared with background stream chemistry predictor variables NH_4^+ , NO_3^- , SRP, and DOC using multiple regression. In multiple regression with V_{f-amb} of SRP and DOC, a reduced number of predictors was used due to small sample size. SRP V_{f-amb} was compared with NH_4^+ , NO_3^- , and DOC, and log-transformed V_{f-amb} of DOC was compared with NO_3^- and DOC. The top models were selected using AICc, which adjusts for small sample sizes. For the incubation experiment, we used a one-way ANOVA to test for differences among the four treatments (birch, birch+ NH_4^+ , acetate at 106C:16N:1P, and acetate at birch C:N:P). If a significant difference was found ($P < 0.05$), we used a Tukey's post-hoc test to determine which treatments were significantly different ($P < 0.05$). We used a linear mixed-effects model accounting for stream as a random effect to compare the effect of DOM stoichiometry and source on N and P uptake efficiency. Data for U_E and V_{f-amb} were natural log transformed to satisfy assumptions of normality before statistical analysis of treatment effects. All statistical analyses were run using R version 0.098.507 with package nlme.

2.4 Results

2.4.1 Physical and chemical conditions

Stream flow was variable across streams, ranging from 12.1 to 87.8 L/s (Table 2.4). DOC concentration was generally low, with a mean of 2.3 mgC/L (Table 2.4). Conductivity of stream water ranged from 56 to 155 $\mu\text{S}/\text{cm}$ and was negatively correlated with nitrate concentration (Spearman's Rank test, $n = 9$, $P < 0.05$, Table 2.5). For all but one stream, nitrate comprised greater than 50% of TDN and ranged from 160 to 628 $\mu\text{gN}/\text{L}$ (Table 2.4). SRP and NH_4^+ concentrations were low, ranging from 0.8 to 4.8 $\mu\text{gP}/\text{L}$ and 8.5 to 37.1 $\mu\text{gN}/\text{L}$, respectively (Table 2.4). SUVA values ranged from 2.34 to 3.39 $\text{L mgC}^{-1} \text{ m}^{-1}$ (Table 2.4), and SUVA was not positively correlated with estimated permafrost extent. For example, the highest SUVA value was found in a stream with low permafrost extent (C2), while the lowest SUVA value occurred in a stream with high permafrost extent (C3). Due to low precipitation over the duration of the experiment, stream chemistry reflects summer baseflow conditions, when groundwater dominates stream flow.

2.4.2 Laboratory incubations

Average DOC losses after 30 days of incubation were 76% for acetate, 77% for birch+ NH_4^+ , and 70% for birch (Fig. 2.2), with birch losing significantly less DOC than all other treatments (ANOVA, $F(3, 8) = 11.83$, $P < 0.05$). SUVA was higher in the birch DOM solution (0.75 $\text{L mgC}^{-1} \text{ m}^{-1}$) than in the acetate solution (0.031 $\text{L mgC}^{-1} \text{ m}^{-1}$), but both sources of DOM had lower SUVA values than those found in the headwater streams of this experiment (mean 2.8 $\text{L mgC}^{-1} \text{ m}^{-1}$, Table 2.4). On day 6, DOC loss was greater in the acetate treatments (mean 73%) compared with the birch DOM (mean 49%, ANOVA, $F(3, 8) = 18.33$, $P < 0.05$, Fig. 2.2), but was not

significantly different from the birch+NH₄⁺ treatment (mean 68.5%). However, DOC loss between day 6 and 30 was greatest from birch (mean 21%, ANOVA, $F(3, 8) = 13.03$, $P < 0.05$, Fig. 2.2). Interestingly, the acetate and birch+NH₄⁺ incubations had similar DOC loss, and the two acetate treatments had similar DOC loss despite having different C:N:P ratios.

2.4.3 Nutrient uptake for single-addition solutes

Ambient uptake lengths for NH₄⁺ and SRP were variable among streams, ranging from 24 to 288 m for NH₄⁺ and 61 to 633 m for SRP (Table 2.4). Uptake lengths for acetate-DOC were similar to those of NH₄⁺ and SRP, ranging from 88 to 301 m (Table 2.4). S_{w-amb} is expected to increase with greater stream flow (Newbold et al. 1981); however, across our streams the range in S_{w-amb} was not correlated with discharge (Spearman's Rank test, $P > 0.05$). Mean V_{f-amb} was similar between acetate-DOC, NH₄⁺, and SRP (Fig. 2.3). Uptake velocities for added nutrients were predicted in part by ambient stream chemistry (Table 2.6), although none of the relationships were statistically significant. For NH₄⁺, ambient SRP concentration was the best predictor for V_{f-amb} , and had a positive effect on V_{f-amb} (Multiple regression, $n = 9$, Adj $R^2 = 0.17$, Fig. 2.4). Reciprocally, ambient NH₄⁺ concentration was the best predictor for V_{f-amb} of SRP (Multiple regression, $n = 7$, Adj $R^2 = 0.25$, Fig. 2.5). DOC V_{f-amb} was best predicted by ambient DOC concentration (Multiple regression, $n = 6$, Adj $R^2 = 0.28$, Fig. 2.6).

2.4.4. Effects of nutrient stoichiometry and DOM source on uptake

For our nutrient stoichiometry hypothesis, we found that varying C:N:P had no measurable effects on U_E of inorganic nutrients. Co-addition of N+P resulted in U_E similar to single additions of NH₄⁺ (Fig. 2.7) for high N:P (Linear Mixed-Effects Model, $t = 1.28$, $df =$

13.3, $P = 0.219$) and low N:P (Linear Mixed-Effects Model, $t = 0.75$, $df = 13.4$, $P = 0.466$). Likewise, U_E of SRP alone was similar to N+P co-addition (Fig. 2.8) at high N:P (Linear Mixed-Effects Model, $t = 1.34$, $df = 9.69$, $P = 0.211$) and low N:P (Linear Mixed Effects Model, $t = -0.58$, $df = 9.39$, $P = 0.577$). In addition, carbon from DOM did not increase U_E of NH_4^+ over N+P co-additions (Linear Mixed-Effects Model, $t = -1.33$, $df = 13.1$, $P = 0.205$) but did increase U_E compared with NH_4^+ added alone, although this difference was not significant (Linear Mixed-Effects Model, $t = -1.96$, $df = 12.46$, $P = 0.072$, Fig. 2.9). For SRP, DOM did not significantly increase U_E compared with SRP added alone (Linear Mixed-Effects Model, $t = -0.27$, $df = 4.45$, $P = 0.801$) or in N+P co-additions (Linear Mixed-Effects Model, $t = -1.26$, $df = 4.51$, $P = 0.268$, Fig. 2.10).

In addressing the carbon source hypothesis, we found that nutrient uptake was similar between DOM additions with either acetate or birch. U_E of NH_4^+ was similar in acetate and birch DOM (Linear Mixed-Effects Model, $t = 1.60$, $df = 11.38$, $P = 0.136$, Fig. 2.11), and also for SRP both DOM types had similar effects on U_E (Linear Mixed-Effects Model, $t = 0.33$, $df = 11.33$, $P = 0.747$, Fig. 2.12).

2.5 Discussion

2.5.1 Nutrient uptake in boreal forest headwater streams

Our two hypotheses were that 1) nutrient stoichiometry and 2) DOM source would affect nutrient uptake. We found that nutrient uptake efficiency (U_E) varied little between additions with N and P alone, N+P, and DOM. We found no significant effect of DOM addition on NH_4^+ U_E , which is surprising when considering that streams of the CPCRW are primarily heterotrophic (Betts and Jones 2009). The effect of added labile DOC increasing NH_4^+ uptake has previously

been reported in small streams (Kirchman et al. 1990, Bernhardt and Likens 2002, Johnson et al. 2009, Blaen et al. 2013). We expected nutrient uptake would respond to labile carbon inputs through increased microbial productivity, but acetate and birch-derived DOM had similar effects on U_E for NH_4^+ (Fig. 2.11) and SRP (Fig. 2.12). This could be a result of both being highly labile carbon sources, as seen in our incubation experiments (Fig. 2.2). Likewise, the stoichiometric ratios in the DOM treatments may not have been different enough for us to detect an effect on NH_4^+ or SRP uptake.

When comparing the effects of nutrient stoichiometry on uptake, varying N:P added in the stream did not affect U_E for N (Fig. 2.7) or P (Fig. 2.8). In contrast, other nutrient addition studies that found interrelationships between stream N and P uptake (O'Brien and Dodds 2010, Schade et al. 2011, Gibson and O'Reilly 2012, Gibson et al. 2015) and an incubation experiment found N and P co-limitation in stream water (Mineau et al. 2013). The apparent decoupling of N and P uptake in boreal forest streams may be explained by greater abiotic uptake of SRP (Mulholland et al. 1990b), in which case P uptake capacity is limited mainly by available sediment binding sites, or our nutrient additions may have been too short-term to detect an effect of N+P co-addition. In the Kuparuk River in arctic Alaska, P enrichment increased algal growth, showing that P was limiting in-stream primary productivity (Peterson et al. 1985). Comparing uptake velocity of added N, P, and DOC with stream ambient chemistry revealed some patterns that may link N and P uptake. V_{f-amb} of NH_4^+ was weakly positively correlated with ambient SRP (Fig. 2.4), suggesting that P availability could limit N uptake. However, V_{f-amb} of SRP was weakly negatively associated with ambient NH_4^+ (Fig. 2.5), suggesting that the mechanism limiting P uptake is different from that limiting N.

DOC loss from acetate and birch DOM in our incubation that was greater than 70% over 30 days revealed that both were sources of labile organic carbon (Fig. 2.2). In comparison, lability of DOC in boreal forest stream water ranges from 2 to 35% over 40 days (Balcarczyk et al. 2009). The loss of DOC from birch in our incubation was similar to a previous result that found 60% of DOC in birch leachate was mineralized over a month (Wickland et al. 2007). Within our incubation, inorganic N increased the initial and total loss of DOC from the birch treatment compared with unamended birch (Fig. 2.2). Another DOM incubation experiment has found that the addition of NH_4^+ stimulated microbial consumption of DOC from maple leaves (Mineau et al. 2013). However, we did not see the same result in our in-stream nutrient additions; instead, we found that acetate U_E was unaffected by inorganic N and P, a result also found in a study of forested streams in Michigan (Johnson et al. 2009). The contrasting results between our incubation and in-stream nutrient additions may reflect changes in microbial response with DOC availability, where the initial concentration of labile DOC was greater in the incubation (12 mgC/L) than during the TASCC additions (approximately 2 mgC/L increase above ambient). In boreal forest streams, DOC demand may be independent of N and P concentration when labile carbon limits heterotrophic activity.

We predicted that ambient stream chemistry would affect nutrient uptake due to differential availability of inorganic and organic substrates. The headwater streams of the CPCRW have high nitrate (NO_3^-) concentration relative to other streams with low anthropogenic and atmospheric inputs of N (Jones et al. 2005). Nitrate may be utilized as a source of inorganic N in streams, which could affect NH_4^+ uptake. In boreal forest streams, there was no detectable relationship between ambient NO_3^- and V_{f-amb} of NH_4^+ , but NO_3^- was weakly negatively correlated with V_{f-amb} of SRP (Table 2.6). In temperate headwater streams, increases in DOC

uptake have been reported with the addition of NO_3^- (Brookshire et al. 2005). Reciprocally, added acetate DOC has increased NO_3^- uptake (Hedin et al. 1998, Bernhardt and Likens 2002). Despite high NO_3^- concentration in these streams, we did not find a relationship between ambient NO_3^- and DOC uptake. During DOM additions, ambient NO_3^- concentration did not change despite high uptake of acetate-DOC, suggesting that other sources of N, such as NH_4^+ added with the DOM, may have been preferentially assimilated.

Ammonium flux through watersheds will also likely be affected by changes in watershed flow path depth. Tundra warming experiments show that warmer soils increase the rate of microbial N mineralization (Chapin et al. 1995, Hartley et al. 1999), potentially generating more NH_4^+ in soils available for transport to streams. Shallow soils exhibit the greatest uptake of inorganic N when compared with deeper soils (Harms and Jones 2012) that are below the main rooting zone of plants and have relatively lower microbial activity. Thus, seasonal increases in thaw depth may result in decreased uptake of NH_4^+ and NO_3^- and lead to increased export of inorganic N via deeper catchment flowpaths (Harms and Jones 2012). Greater N availability could positively affect DOM mineralization and respiration, like the results from our incubation that showed that birch leachate lost as much carbon as acetate when amended with NH_4^+ (Figure 2.2). In multiple regression, increasing NH_4^+ had a weakly negative correlation with SRP V_{f-amb} (Fig. 2.5), while greater SRP availability had a weakly positive correlation with NH_4^+ V_{f-amb} (Fig. 2.4). This result is surprising given that N and P have been found to co-limit productivity in other stream ecosystems, and suggests that inorganic N is not limiting P uptake in boreal forest streams.

Despite greater total N concentration in streams with little permafrost, flux of dissolved organic nitrogen (DON) was not related to catchment permafrost extent in the CPCRW (Jones et

al. 2005) and predictions are variable as to future trends in DON export. Groundwater has lower DON concentration than surface flows, which should lead to a decrease in DON export should stream groundwater discharge increase (Walvoord and Striegl 2007). However, examination of broad geographic trends in DON for Alaska and Siberia suggest that DON flux in boreal and arctic watersheds could increase with future climate warming (Frey and McClelland 2009). DON may contribute to DOM lability in high latitude ecosystems, as the concentration of amino acid-like components in DOM is positively correlated with microbial consumption of DOC (Balcarczyk et al. 2009, Fellman et al. 2009).

2.5.2 Comparing uptake in boreal forest streams with other stream ecosystems

Values for V_{f-amb} of NH_4^+ , SRP, and DOC in our study suggest a high demand for nutrients in boreal forest headwater streams compared with other ecosystems (Table 2.7). In boreal forest streams, median V_{f-amb} of NH_4^+ (9.7 mm/min) and SRP (11.3 mm/min) is higher than in a synthesis of previously published nutrient uptake studies (Ensign and Doyle 2006), where the median for NH_4^+ and SRP V_f in headwater streams was 6.8 and 2.8 mm/min, respectively. Values for acetate-DOC V_{f-amb} in boreal forest streams (median 9.4 mm/min) are within the range previously published in the literature (Table 2.7). With the inclusion of recent studies of nutrient uptake in high latitude streams, the literature range in V_f encompasses 0.4 – 119.4 mm/min for NH_4^+ , 0.09 – 55.3 mm/min for SRP, and 1.0 – 28.7 mm/min for acetate-DOC (Table 2.7). Some reported values are from studies with experimentally elevated nutrient concentrations, which underestimates V_{f-amb} . Notably, high NH_4^+ V_f was measured in the Kuparuk River in arctic Alaska (119.4 mm/min, Wollheim et al. 2001) in a reach that has been part of a long-term P fertilization experiment. High autotrophic productivity in the Kuparuk after

P addition may have increased inorganic N demand. The range in V_f of NH_4^+ (Figure 2.13A), SRP (Figure 2.13B), and DOC (Figure 2.13C) is surprisingly similar across different latitudes, with some of the highest values for V_f reported in high latitude streams.

Low ambient nutrient concentration in high latitude streams may explain the greater demand for nutrients than in streams of temperate regions, which may also have been influenced by anthropogenic inputs of N or P. Because V_f can decline non-linearly with increasing nutrient concentration, following Michaelis-Menten kinetics (Payn et al. 2005), a small difference in stream nutrient concentration could have a significant impact on nutrient demand. In light of this, it is interesting that NH_4^+ demand was high in these boreal forest streams, which have elevated NO_3^- concentration despite being relatively pristine. Ammonium is a preferred form of nitrogen for microorganisms (Dortch 1990) because it is energetically less expensive to assimilate than nitrate (Hildebrand 2005), which may explain why NH_4^+ demand remained high. Temperature is another abiotic factor that can influence rates of nutrient uptake (Rasmussen et al. 2011), and it is notable that V_f in boreal forest streams is comparable to V_f in warmer, temperate streams. For example, median V_f of NH_4^+ in a tropical stream in Puerto Rico (10.1 mm/min, Merriam et al. 2002) is close to the median V_f of NH_4^+ in this study (9.7 mm/min), suggesting that stream nutrient demand is not necessarily greater in regions with warmer annual temperatures and higher irradiance.

2.5.3 Consequences of changing stream chemistry for nutrient uptake

Predicting how boreal stream carbon and nutrient cycling will be affected by a loss of discontinuous permafrost is complicated by biotic and hydrologic variables such as changes in DOM source, terrestrial processing of DOM and the resulting lability of carbon in streams,

changes in flowpaths of water through catchments and resulting stream discharge. The results from this study do not support the notion that DOM affects nutrient uptake, but stream nutrient concentration may affect DOM lability, as seen in the enhanced loss of DOC from birch DOM in the incubation with added NH_4^+ (Fig. 2.2). While we found no effect of instantaneous manipulation of stream water stoichiometry on uptake, a long-term change in stream chemistry, such as the Kuparuk River phosphorus fertilization experiment (Peterson et al. 1985), might reveal an effect on nutrient cycling.

In the CPCRW, stream chemistry reflects estimated permafrost extent. For example, DOC concentration and aromaticity increase (Petrone et al. 2006) with extent of permafrost, and in streams with little or no permafrost N concentrations exceed atmospheric inputs, the majority of which is nitrate (Jones et al. 2005). As a result, changes in permafrost extent will alter stream chemistry (Fig. 2.14), possibly with consequences for nutrient uptake. Compared with streams in catchments underlain by extensive permafrost, where flowpaths are restricted to shallow organic soil, the DOC in groundwater-fed streams shows characteristics of a more labile carbon source (O'Donnell et al. 2012) with lower aromaticity (Balcarczyk et al. 2009), suggesting that stream water DOC composition may change as permafrost retreats. However, total DOC concentration is generally lower in streams with little permafrost (Petrone et al. 2006). If input of inorganic nutrients from groundwater increases but the concentration of available DOM declines, streams may become less retentive of inorganic nutrients (Fig. 2.14, panel B). In contrast, increased DOM lability could stimulate heterotrophic productivity, such as assimilation, respiration, and mineralization (Fig. 2.14, panel C). Heterotrophic mineralization of DOM could have a positive effect on stream autotrophic productivity, if light is not limiting. In this scenario, microbial

uptake increases carbon and nutrient retention in the stream, and respiration of DOC and NO_3^- increases (Fig. 2.14, panel C).

2.5.4 Conclusions

Future permafrost loss may increase inorganic nutrient export (McClelland et al. 2007) and decrease DOC export to boreal forest streams (O'Donnell et al. 2012). Observations from Alaskan watersheds show that although DOC concentration in stream water decreases with permafrost loss, the proportion of DOC that is labile may increase (O'Donnell et al. 2012). The results from this study do not conclusively identify whether DOC, N, or P will be the main control on nutrient spiraling in boreal forest streams. Median V_{f-amb} of 9.7 mm/min for NH_4^+ , 11.3 mm/min for SRP, and 9.4 mm/min for DOC suggest that all three solutes are in high demand. High nutrient demand has previously been measured in other high latitude stream ecosystems, and if permafrost loss and warming temperatures in the boreal forest increase the flux of inorganic nutrients and labile DOM to streams, nutrient uptake and productivity may increase in response. In the results of this study, stream nutrient uptake remained high despite changing stoichiometry and organic carbon source; thus, if flux of inorganic nutrients to streams increases with changes in permafrost extent, nutrient uptake may increase in boreal forest headwater streams.

2.6 Figures

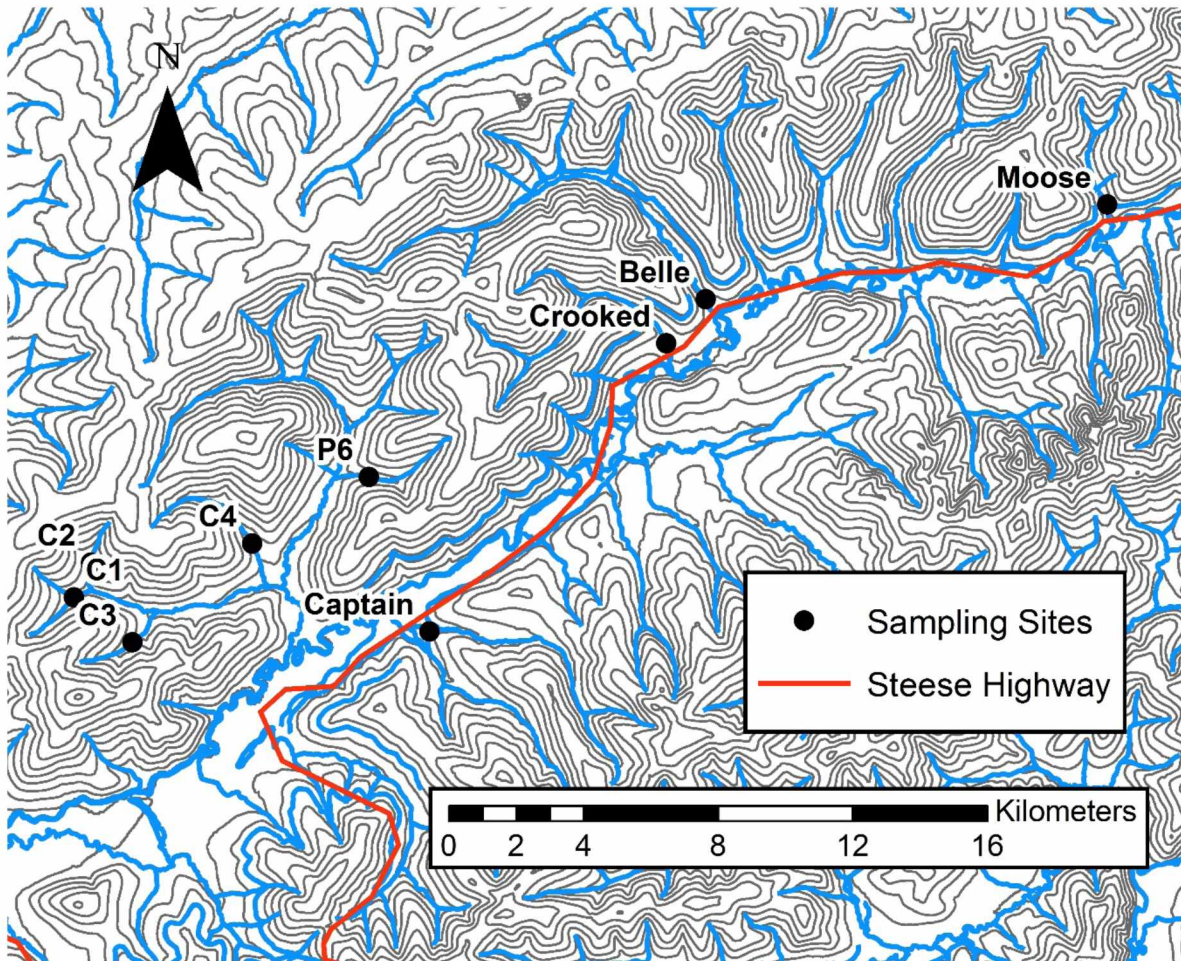


Figure 2.1. Location of study streams within the Caribou-Poker Creeks Research Watershed and along the Steese Highway, 50 km NE of Fairbanks, Alaska.

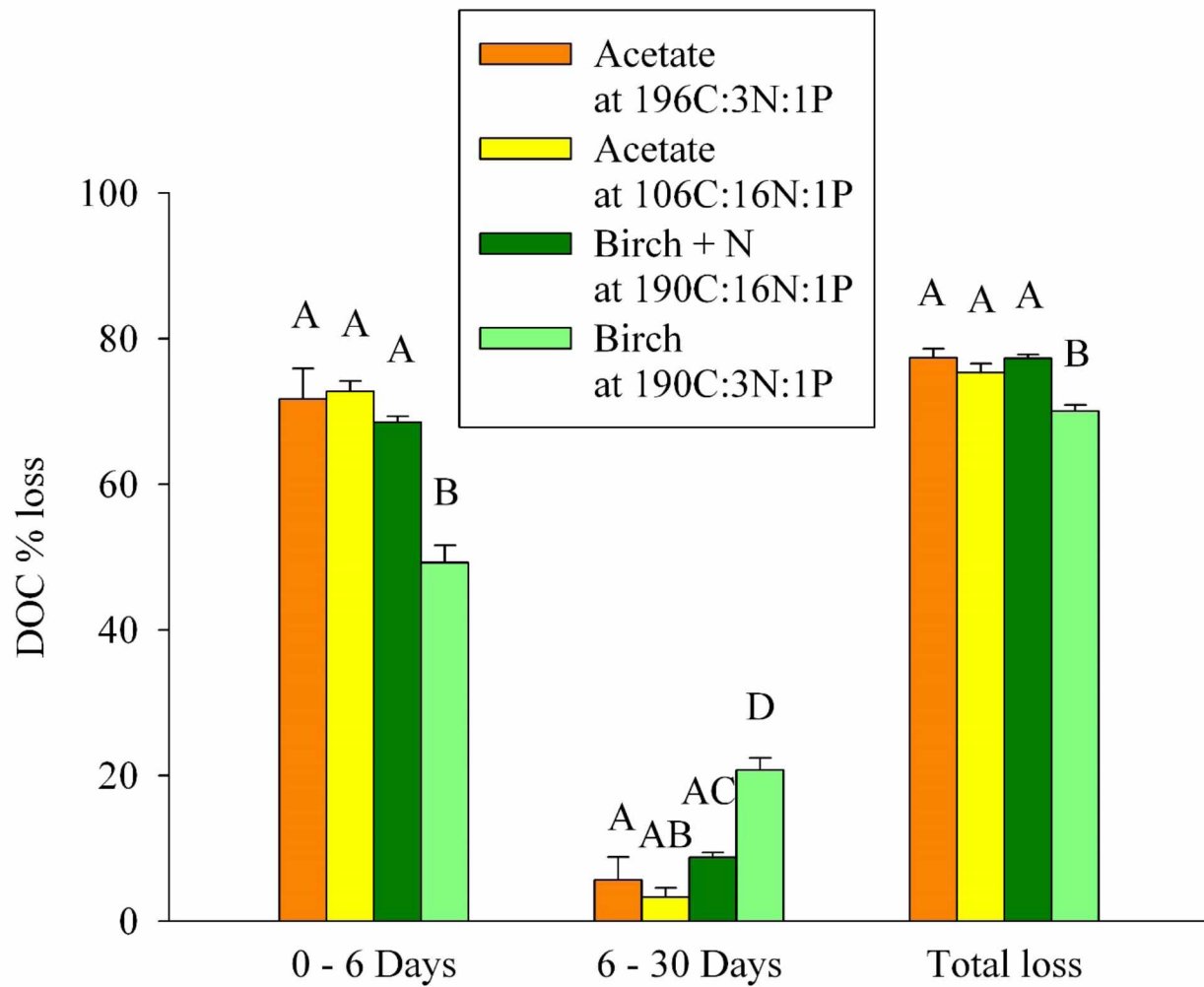


Figure 2.2. Biodegradable DOC of acetate and birch DOM, with and without nutrient addition, was measured as DOC loss during 6 and 30 days of laboratory incubation. Letters denote significant differences between treatments (see text for full statistical results), and error bars represent \pm SE.

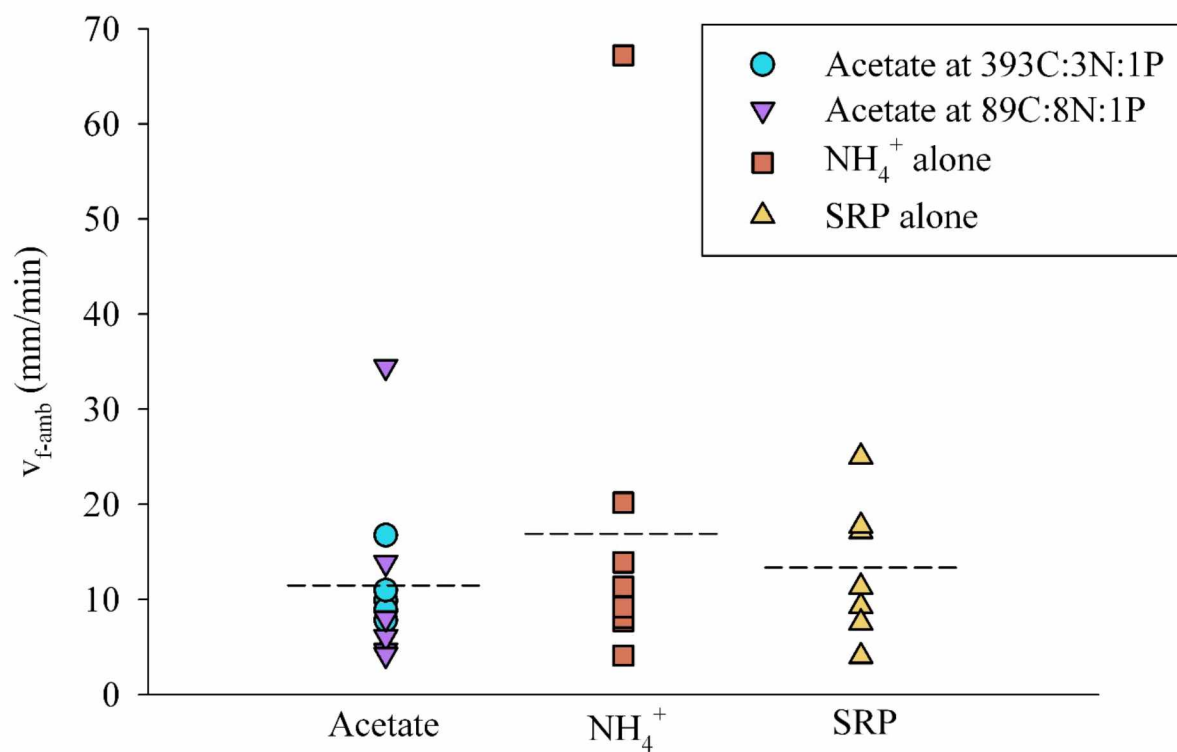


Figure 2.3. V_{f-amb} of acetate-DOC at 89C:8N:1P and 393C:3N:1P, NH_4^+ , and SRP. Dashed lines represent the mean.

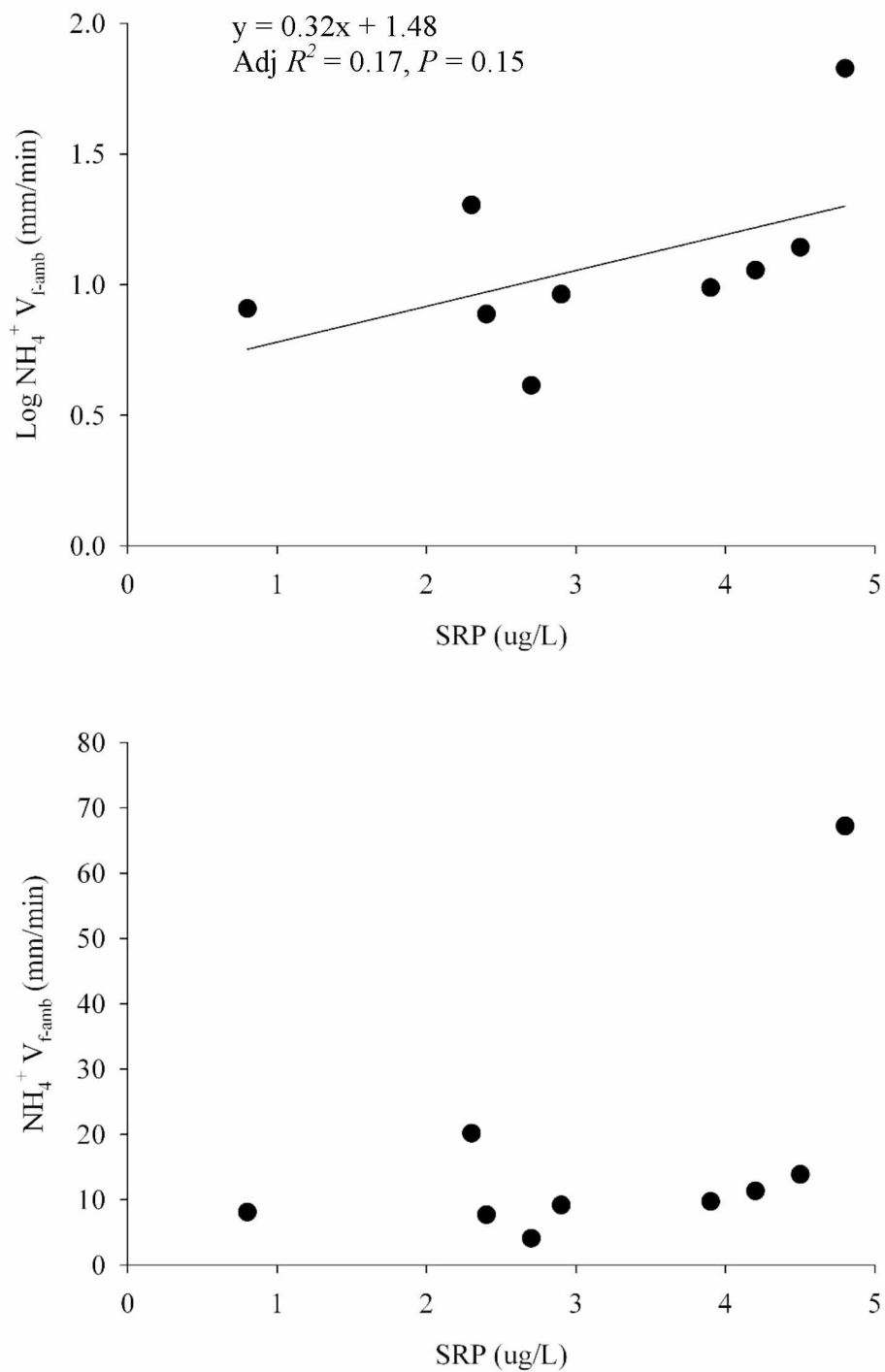


Figure 2.4. $V_{f\text{-}amb}$ of NH_4^+ compared with stream ambient SRP concentration. Note that the upper panel presents $V_{f\text{-}amb}$ log-transformed and the lower panel presents $V_{f\text{-}amb}$ untransformed.

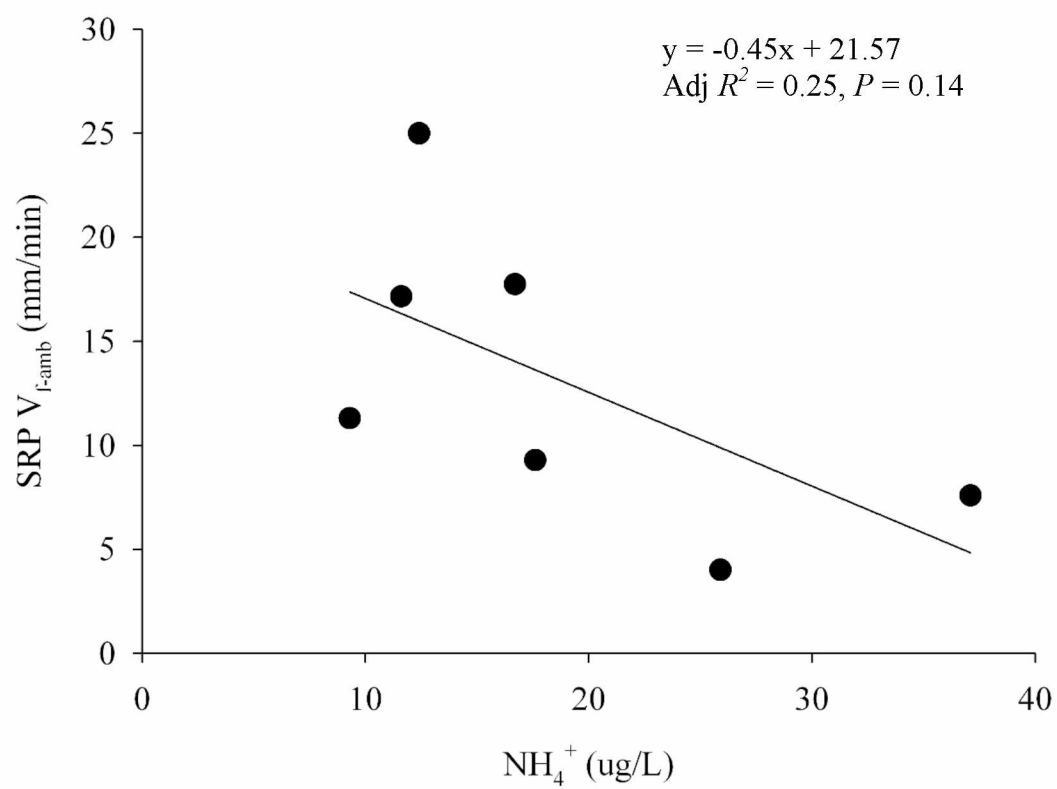


Figure 2.5. V_{f-amb} of SRP compared with stream ambient NH_4^+ concentration.

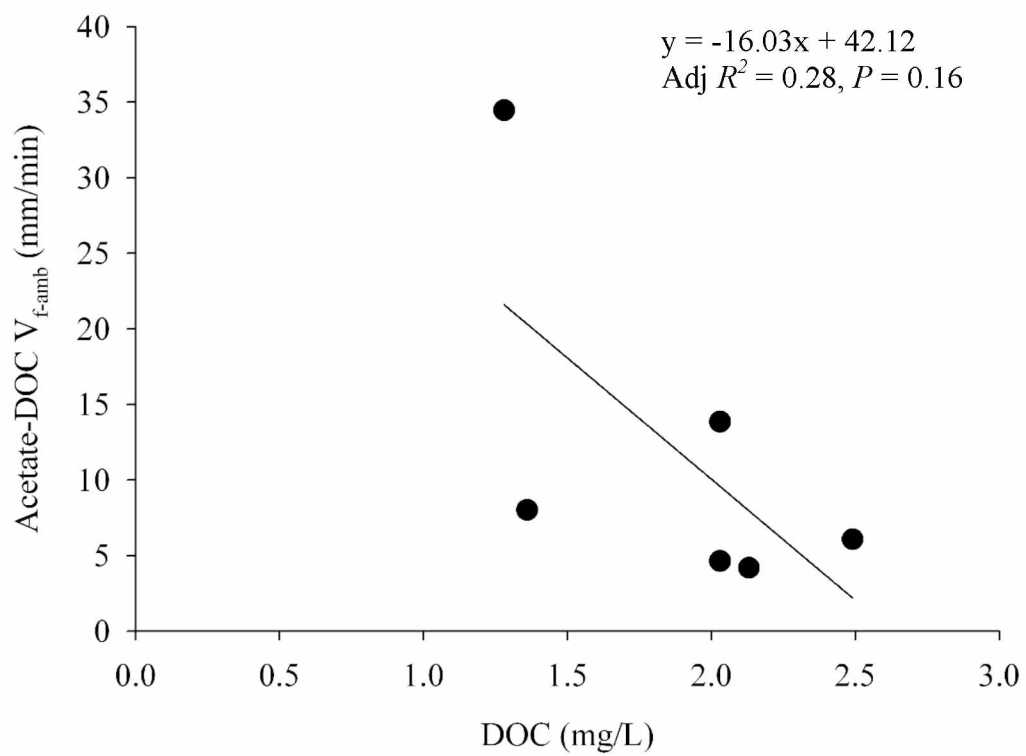


Figure 2.6. V_{f-amb} of acetate-DOC compared with stream ambient DOC concentration.

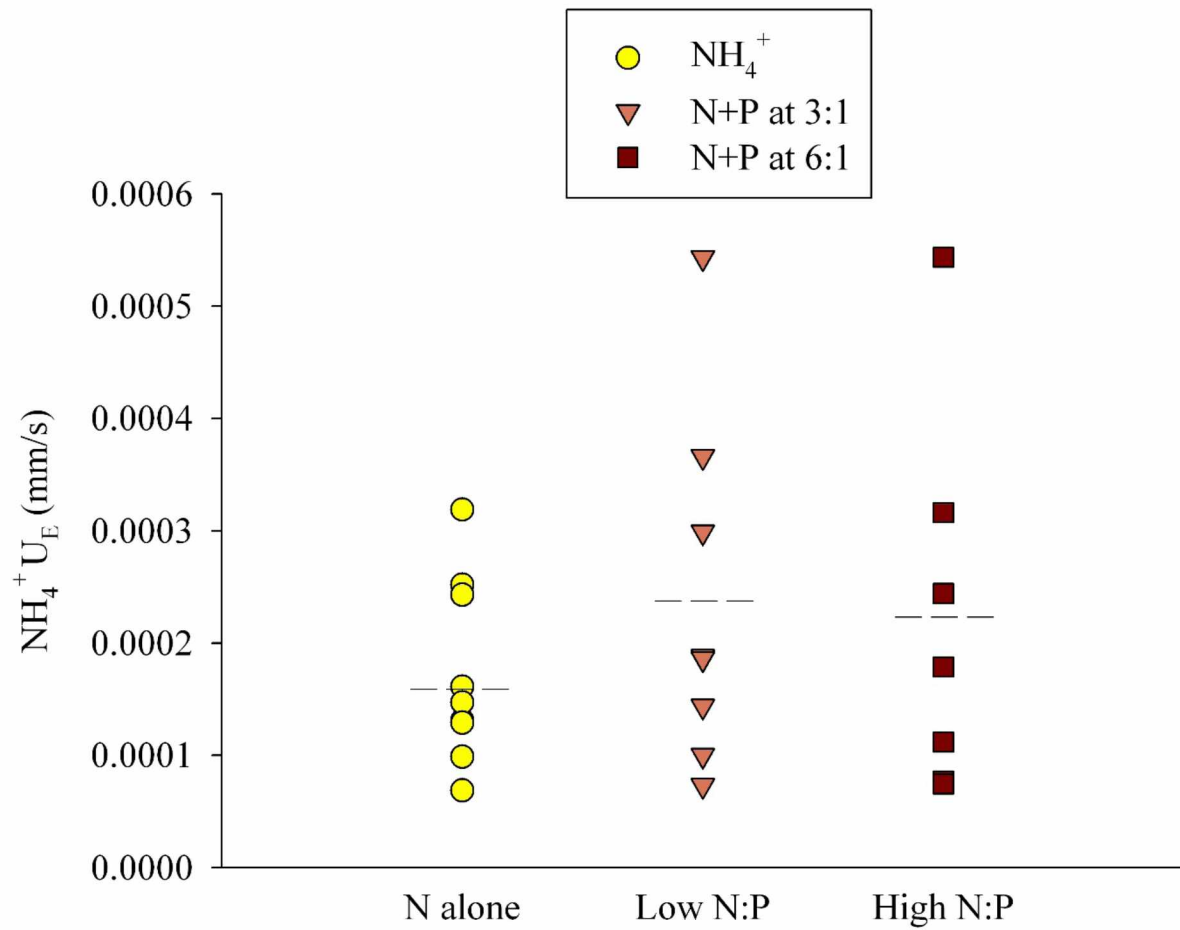


Figure 2.7. U_E (the slope of the response in areal uptake, U , with increasing nutrient concentration) of NH_4^+ for additions of N alone and N+P at two ratios. Dashed lines represent the mean. A mixed-effects model found no significant differences (see text for full statistical results).

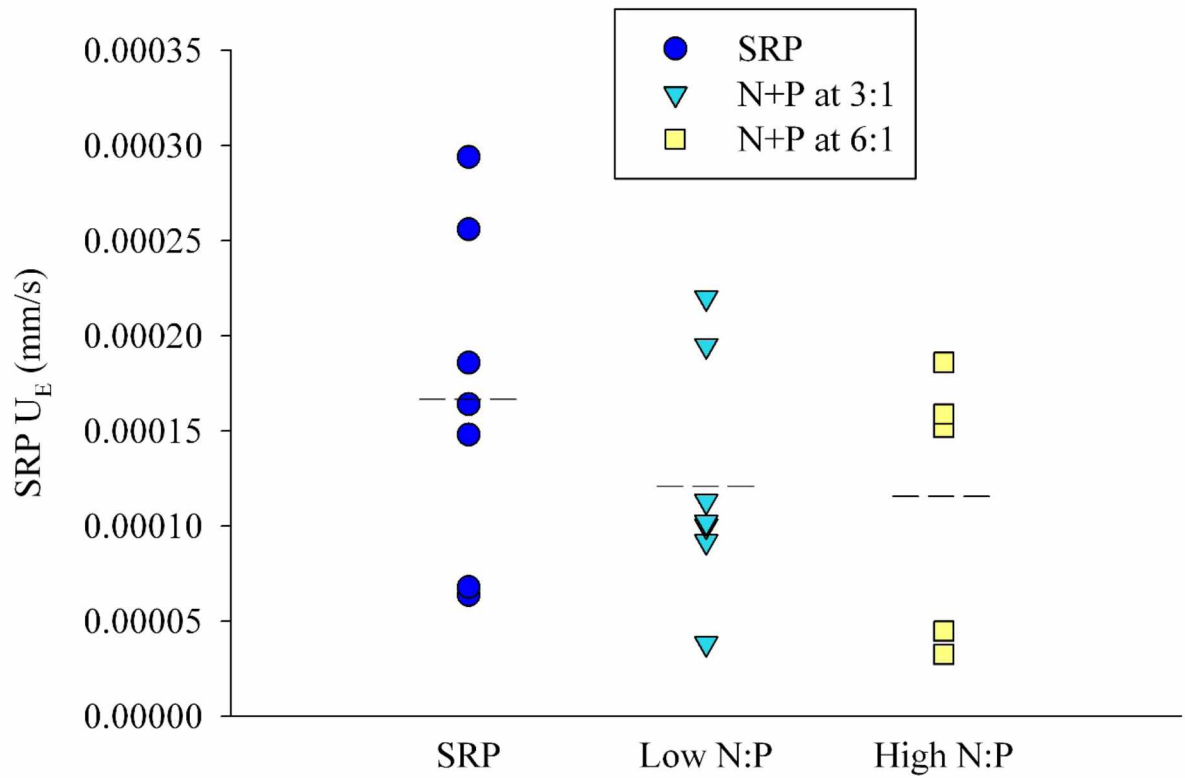


Figure 2.8. U_E (the slope of the response in areal uptake, U , with increasing nutrient concentration) of SRP for additions of SRP alone and N+P at two ratios. Dashed lines represent the mean. A mixed-effects model found no significant differences (see text for full statistical results).

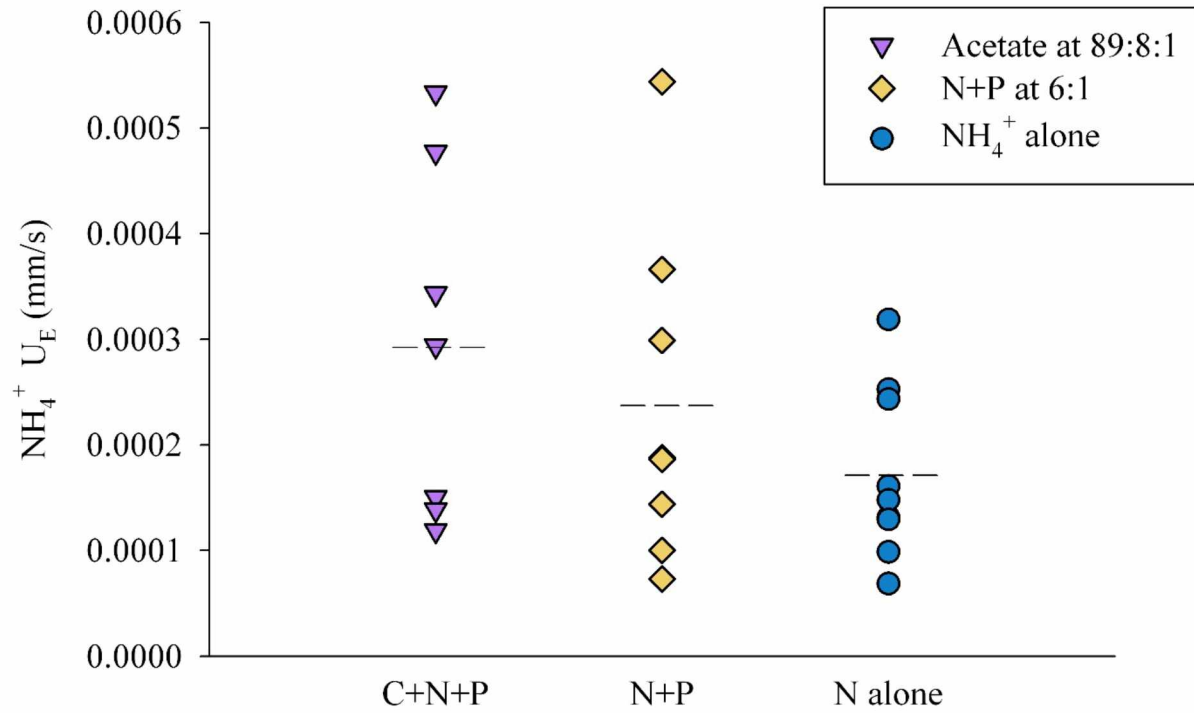


Figure 2.9. U_E (the slope of the response in areal uptake, U , with increasing nutrient concentration) of NH_4^+ for N alone, N+P, and C+N+P additions. Dashed lines represent the mean. A mixed-effects model found no significant differences (see text for full statistical results).

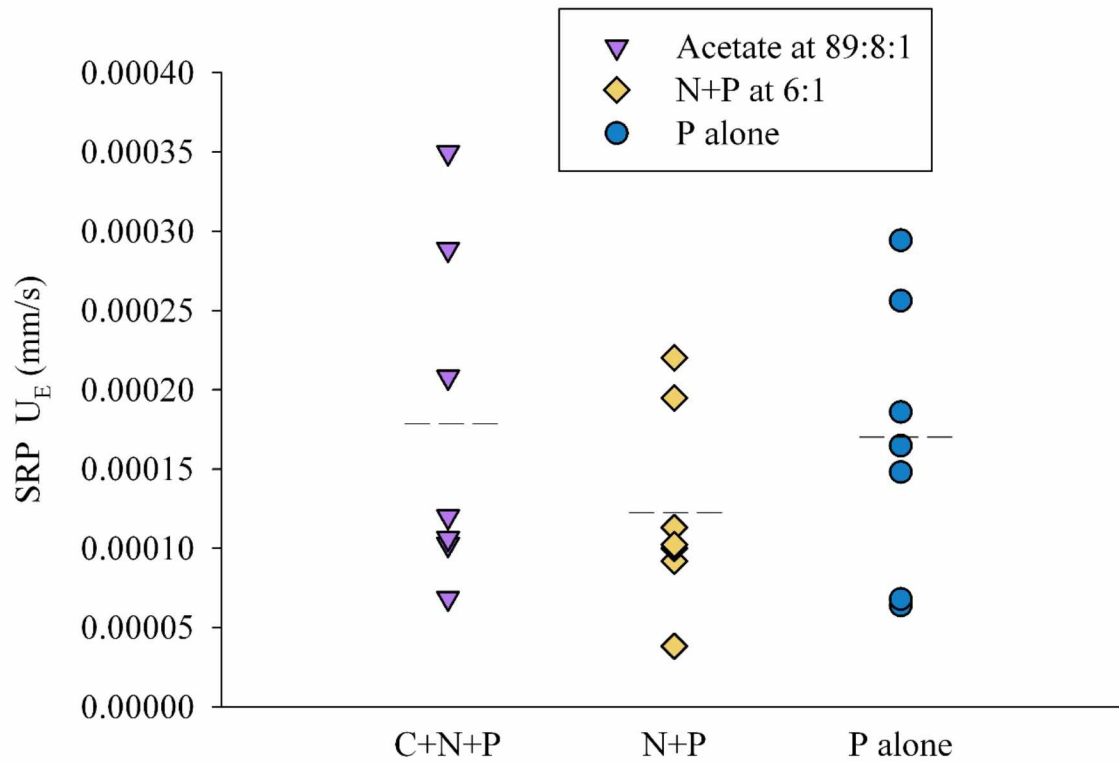


Figure 2.10. U_E (the slope of the response in areal uptake, U , with increasing nutrient concentration) of SRP for P alone, N+P, and C+N+P additions. Dashed lines represent the mean. A mixed-effects model found no significant differences (see text for full statistical results).

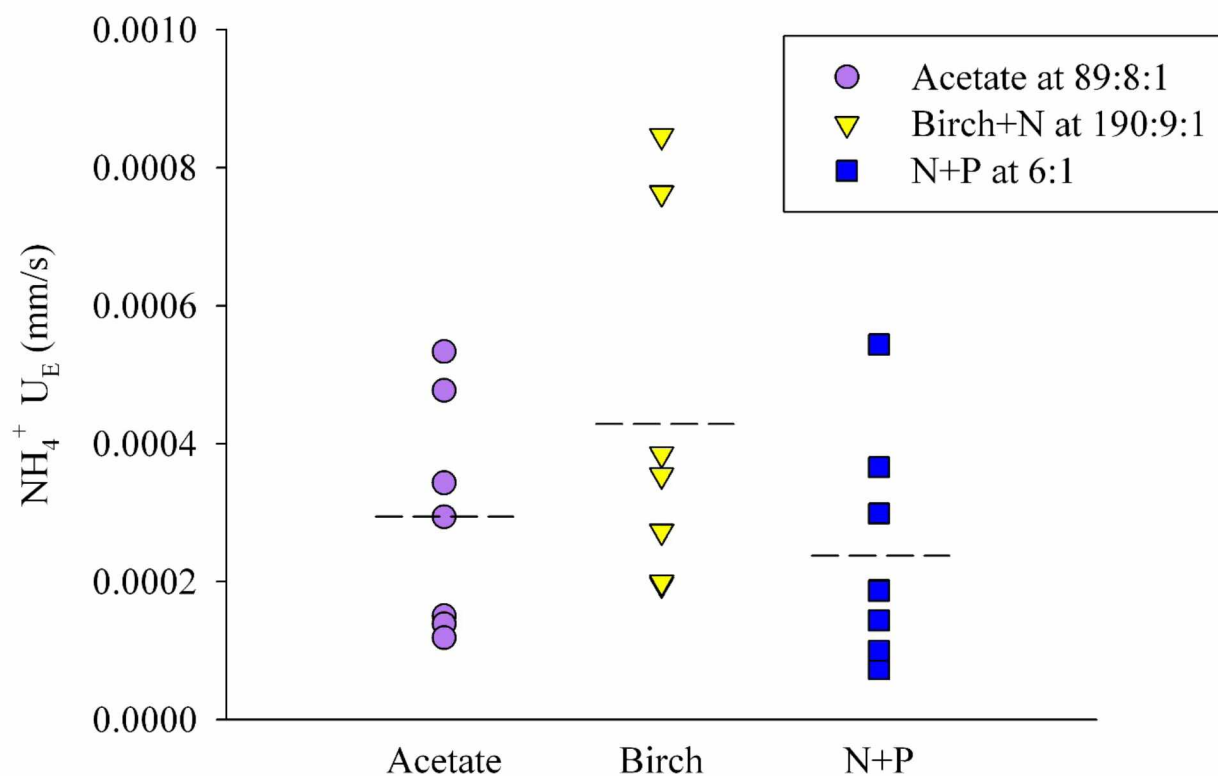


Figure 2.11. U_E (the slope of the response in areal uptake, U , with increasing nutrient concentration) of NH_4^+ with acetate and birch DOM. Dashed lines represent the mean. A mixed-effects model found no significant differences (see text for full statistical results).

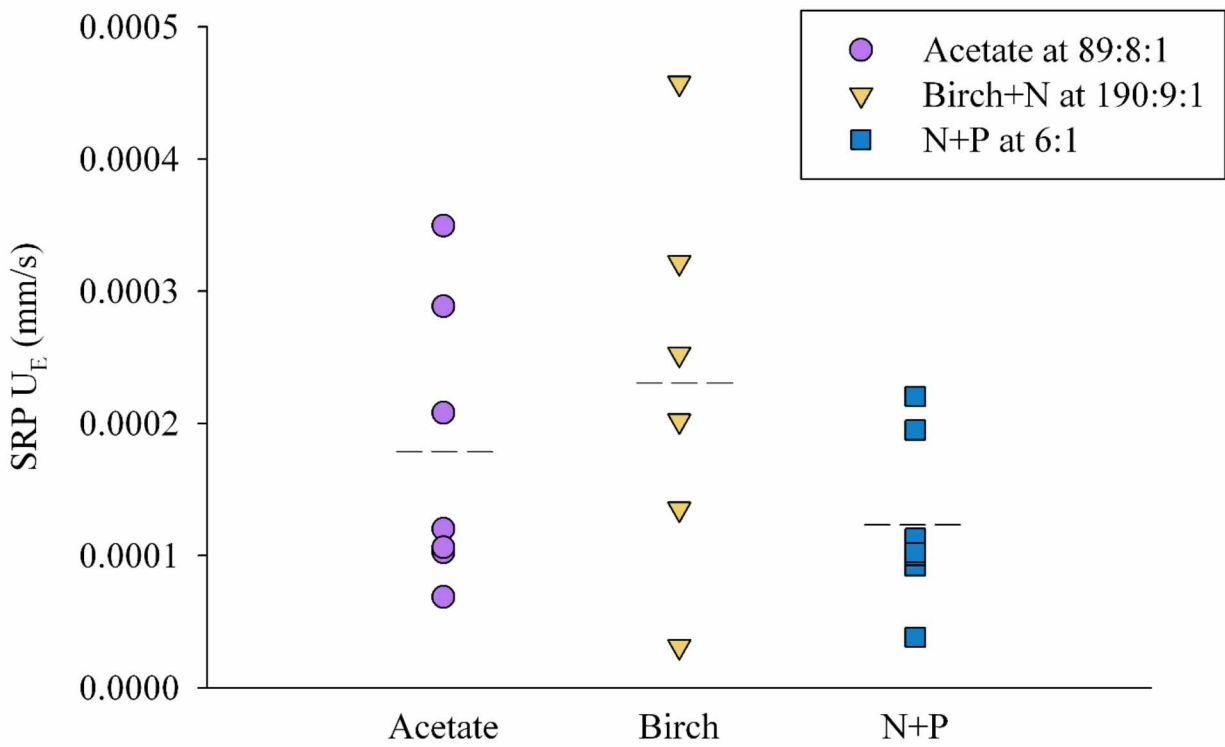
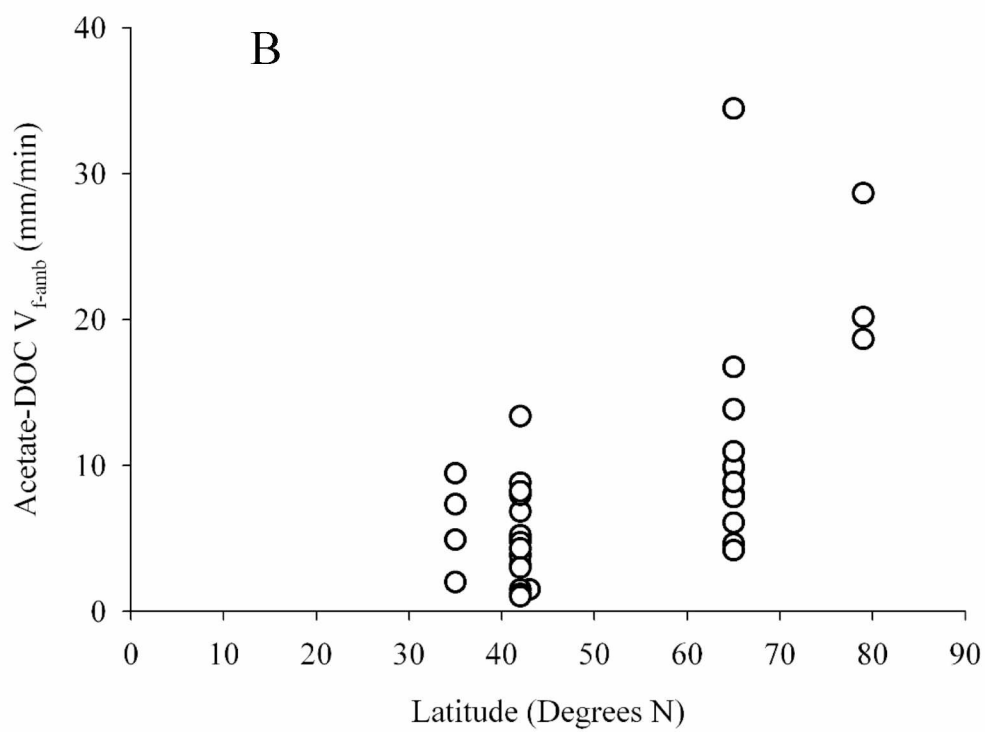
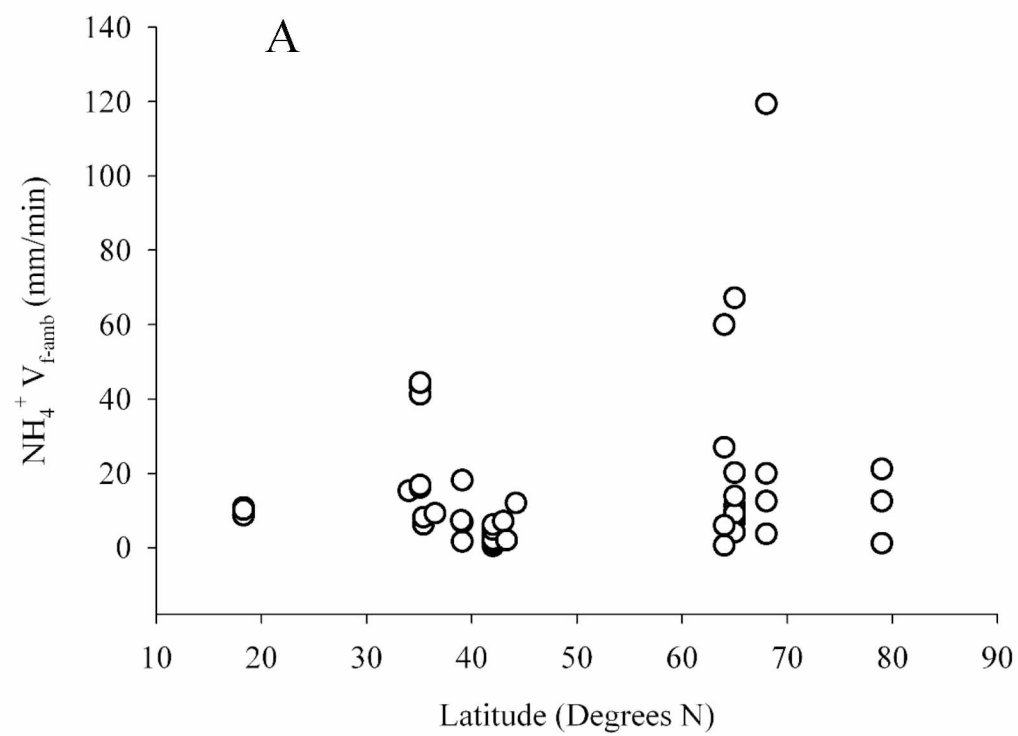


Figure 2.12. U_E (the slope of the response in areal uptake, U , with increasing nutrient concentration) of SRP with acetate and birch DOM. Dashed lines represent the mean. A mixed-effects model found no significant differences (see text for full statistical results).



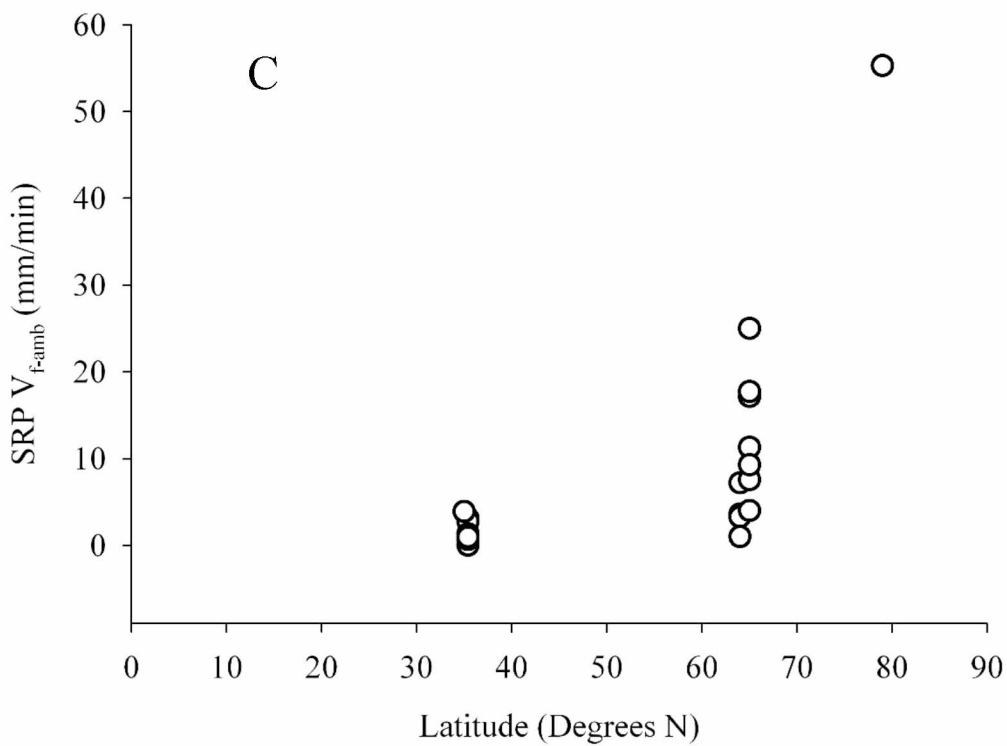


Figure 2.13. V_{f-amb} values for NH_4^+ (A), DOC (B), and SRP (C) from the literature and this study, arranged according to stream latitude.

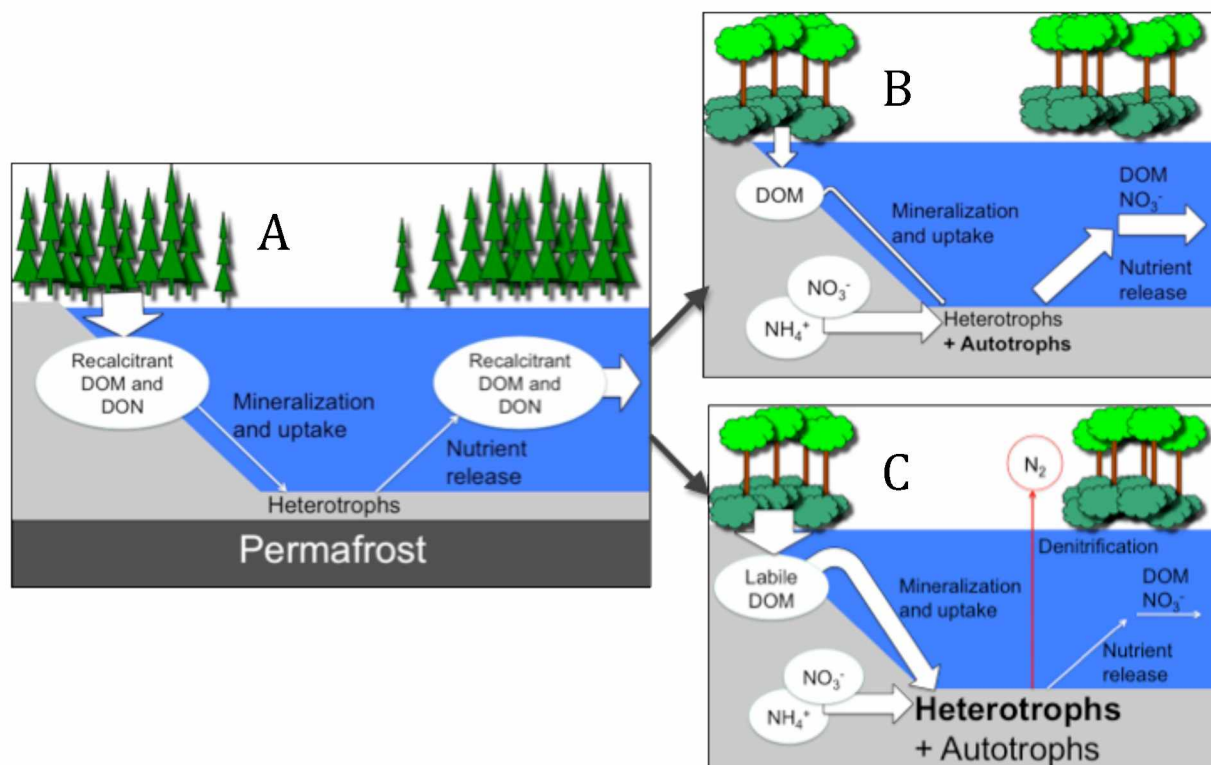


Figure 2.14. Implications of permafrost loss for stream productivity and nutrient cycling (see the Discussion for a full description of the conceptual model). Panel A depicts the current status of streams underlain by permafrost, where spruce forests with thick organic soil leach relatively recalcitrant DOM and DON into streams. Panel B shows a scenario of permafrost loss where DOM inputs to streams decrease while inorganic nutrient flux to streams increases. Panel C shows a scenario of permafrost loss where inputs of labile DOM to streams increase concurrently with increases in inorganic nutrient inputs.

2.7 Tables

Table 2.1. Composition of the DOM additions, with C:N:P presented in molar ratios. For the birch at low C:N, additional ammonium was added in the form of ammonium chloride.

DOM Additions					
Carbon Source	C:N	Nutrient Ratios	Target DOC (gC/L)	Target N (mgN/L)	Target P (mgP/L)
Acetate	High	89C:8N:1P	12	1067	132
Acetate	Low	393C:3N:1P	12	94	77
Birch	High	190C:3N:1P	14	232	192
Birch	Low	190C:9N:1P	14	792	192

Table 2.2. Composition of the inorganic nutrient additions, with N:P presented in molar ratios.

N and P Additions			
	Target N:P	NH ₄ ⁺ (gN/L)	SRP (gP/L)
N or P alone	N/A	20	20
Low N:P	6:1	20	6.7
High N:P	35:1	20	1.2

Table 2.3. Composition of solutions for bioavailability of acetate and birch DOM, with C:N:P presented in molar ratios. For the birch+N treatment, additional ammonium was added in the form of ammonium chloride.

DOM Bioavailability Incubations				
Treatment	Target C:N:P	DOC (mgC/L)	N ($\mu\text{gN/L}$)	P ($\mu\text{gP/L}$)
Birch	190:3:1	14	232	192
Birch+N	190:16:1	14	1362	192
Acetate at Birch C:N:P	196:3:1	12	214	158
Acetate at Redfield C:N:P	106:16:1	12	2112	292

Table 2.4. Background water chemistry for study streams. Data are presented as means \pm SE, $n \geq 3$.

Stream Chemistry									
Stream Site	Date	Reach Length (m)	Width (m)	Discharge (L/s)	Velocity (m/s)	DOC (mgC/L)	Conductivity (μ S/cm)	SRP (μ gP/L)	SUVA (L mgC ⁻¹ m ⁻¹)
C1	7/4/13	83	0.8 \pm 0.1	25.2 \pm 4.6	0.47 \pm 0.01	2.49 [†]	56.2 \pm 0.7	3.9 \pm 0.7	3.11 [†]
C2	7/4/13	100	0.6 \pm 0.0	18.9 \pm 1.1	0.83 \pm 0.00	2.03 \pm 0.04	75.2 \pm 0.5	4.2 \pm 0.6	3.39 [†]
C3	7/11/13	100	0.7 \pm 0.1	15.3 \pm 0.2	0.53 \pm 0.02	4.88 [†]	74.7 \pm 1.2	0.8 \pm 0.3	2.34 [†]
C4	7/14/13	80	0.7 \pm 0.1	31.3 \pm 3.0	0.62 \pm 0.02	1.36 \pm 0.03	98.2 \pm 0.7	2.9 \pm 0.3	2.41 [†]
P6	8/2/13	100	0.8 \pm 0.1	19.2 \pm 1.0	0.57 \pm 0.01	2.31 \pm 0.03	121.3 \pm 1.0	4.5 \pm 0.6	2.93 [†]
Captain	6/30/13	87	3.0 \pm 0.2	80.0 \pm 10.9	0.94 \pm 0.04	2.72 \pm 0.24	179.4 \pm 1.5	4.8 \pm 0.1	3.18 \pm 1.15
Crooked	7/2/13	172	2.6 \pm 0.2	45.5 \pm 0.2	1.48 \pm 0.03	2.13 \pm 0.00	107.8 \pm 0.1	2.7 \pm 0.4	2.92 \pm 0.38
Belle	7/2/13	107	3.7 \pm 0.2	74.7 \pm 1.6	1.41 \pm 0.03	2.03 \pm 0.17	155.5 \pm 0.0	2.4 \pm 0.2	2.49 \pm 0.18
Moose	7/19/13	90	0.4 \pm 0.0	28.0 \pm 1.0	0.57 \pm 0.01	1.28 \pm 0.03	111.8 \pm 0.4	2.3 \pm 0.8	2.73

[†] Sample value from CPCRW baseline data, collected via autosampler from stream reach on injection date.

Table 2.4 Continued.

Stream Site	NH ₄ -N (µgN/L)	NO ₃ -N (µgN/L)	TDN (µgN/L)	S_{w-amb} NH ₄ ⁺ (m)	S_{w-amb} SRP (m)	S_{w-amb} Acetate-DOC (m)	V_{f-amb} NH ₄ ⁺ (mm/min)	V_{f-amb} SRP (mm/min)	V_{f-amb} Acetate-DOC (mm/min)
C1	12.4 ± 1.9	266.3 ± 0.0	370.0 [†]	184	72	239 [‡] ± 56	9.7	25	7.9 [‡] ± 1.9
C2	8.5 ± 0.9	307.1 ± 42.6	710.0 [†]	288	-	227 [‡] ± 63	11.4	-	10.8 [‡] ± 3.0
C3	37.1 ± 2.6	348.4 ± 5.5	510.0 [†]	164	175	134	8.1	7.6	9.9
C4	25.9 ± 1.9	627.5 ± 2.9	707.0 ± 4.3	276	633	301 [‡] ± 15	9.2	4.0	8.9
P6	17.6 ± 1.9	226.7 [†]	274.0 ± 6.1	107	159	88	13.9	9.3	16.8
Captain	19.0 ± 0.5	160.2 ± 3.4	200.2 ± 29.0	24	-	-	67.2	-	-
Crooked	11.6 ± 0.8	250.9 ± 6.5	340.2 [†]	254	61	172 [‡] ± 77	4.1	17.2	7.6 [‡] ± 3.4
Belle	9.3 ± 0.7	199.6 ± 7.2	329.0 [†]	157	131	261	7.7	11.3	4.6
Moose	16.7 ± 1.5	290.9 ± 8.9	274.0 ± 6.1	200	228	117	20.2	17.7	34.5

[†] Sample value from CPCRW baseline data, collected via autosampler from stream reach on injection date.

[‡] $n = 2$ acetate additions

- = No uptake detected

Table 2.5. Correlation matrix for ambient stream chemistry ($n = 9$).

	DOC	Conductivity	SRP	Discharge	SUVA	NO ₃ -N	NH ₄ -N	DIN:SRP
1 DOC (mgC/L)								
2 Conductivity (μS/cm)	0.05							
3 SRP (μgP/L)	0.23	-0.05						
4 Discharge (L/s)	-0.12	0.68	-0.27					
5 SUVA (L mgC ⁻¹ m ⁻¹)	0.05	-0.03	0.30	0.05				
6 NO ₃ -N (mgN/L)	-0.35	-0.73	0.23	-0.61	-0.42			
7 NH ₄ -N (μgN/L)	0.47	0.18	0.50	-0.07	-0.40	0.15		
8 DIN:SRP	-0.18	-0.17	-0.90	0.25	-0.45	0.02	-0.38	
9 DOC:DON	0.69	0.45	0.29	0.14	-0.02	-0.40	0.74	-0.43

Note: Correlations in **bold** denote significance ($P < 0.05$), using Spearman's rank test.

Table 2.6. Summary of multiple regression analysis for variables predicting V_{f-amb} for NH_4^+ , SRP, and DOC using all subsets regression. AICc was used to discriminate between models and because of the small sample size of the dataset. V_{f-amb} for NH_4^+ and High C:N DOC was log-transformed to satisfy assumptions of normality. Only the top models, with a combined AICc weight of ≥ 0.95 , are presented. The full model for SRP contained NH_4^+ , NO_3^- , and DOC. The full model for NH_4^+ contained NH_4^+ , NO_3^- , DOC, and SRP. The full model for DOC contained NO_3^- and DOC.

Response	Predictors	Model	n	Adj R^2	AICc	P -value	Akaike weight (w_i)
SRP V_{f-amb}	NH_4^+	$y = -0.45*\text{NH}_4^+ + 21.57$	7	0.25	57.1	0.14	0.42
	NO_3^-	$y = -0.03*\text{NO}_3^- + 21.69$	7	0.16	57.92	0.20	0.27
	NO_3^- , NH_4^+	$y = -0.01*\text{NO}_3^- + -0.33*\text{NH}_4^+ + 23.85$	7	0.15	58.42	0.32	0.22
	DOC	$y = -0.97*\text{DOC} + 15.44$	7	0.00	60.22	0.73	0.09
NH_4^+ V_{f-amb}	SRP	$y = 0.32*\text{SRP} + 1.48$	9	0.17	27.98	0.15	0.49
	NO_3^-	$y = -0.002*\text{NO}_3^- + 2.99$	9	0.00	29.95	0.43	0.18
	NH_4^+	$y = 0.01*\text{NH}_4^+ + 2.38$	9	0.00	30.79	0.87	0.12
	DOC	$y = -0.03*\text{DOC} + 2.56$	9	0.00	30.81	0.91	0.12
	NH_4^+ , SRP	$y = 0.04*\text{NH}_4^+ + 0.46*\text{SRP} + 0.31$	9	0.00	32.98	0.19	0.04
DOC V_{f-amb} High C:N	NO_3^-	$y = -0.001*\text{NO}_3^- + 2.62$	6	0.025	16.35	0.35	0.68
	DOC	$y = 0.01*\text{DOC} + 2.31$	6	0.00	17.82	0.92	0.32
DOC V_{f-amb} Low C:N	DOC	$y = -16.03*\text{DOC} + 42.12$	6	0.28	60.05	0.16	0.84
	NO_3^-	$y = -0.001*\text{NO}_3^- + 12.30$	6	0.00	63.35	0.97	0.16

Table 2.7. Values of V_f from previous studies in high latitude and temperate systems. Data adapted from Ensign and Doyle (2006).

Nutrient	Range in V_f (mm/min)	Location	Number of Streams	Data source
NH_4^+	1.6 – 6.8 [‡]	Kings Creek, KS	2	Dodds et al. 2002
	0.4 – 5.3	Kalamazoo River basin, MI	18	Johnson et al. 2009
	2.0 – 41.2 [†]	LINX study streams, USA	9	Webster et al. 2003
	6.2 [†]	Walker Branch, TN	1	Payn et al. 2005
	43.4 [†]	Ball Creek, NC	1	Payn et al. 2005
	16.2 – 44.4 [†]	Upper Ball Creek, NC	1	Tank et al. 2000
	8.7 – 10.8 [†]	Quebrada Bisley, Puerto Rico	1	Merriam et al. 2002
	0.6 – 60.0	Iceland	4	Rasmussen et al. 2011
	1.2 – 21.2	Svalbard	3	Blaen et al. 2013
	12.5 [†]	E1 outlet, AK	1	Webster et al. 2003
	3.7 – 119.4 [†]	Kuparuk River, AK	1	Wollheim et al. 2001
	4.1 – 67.2 [‡]	Boreal streams, AK	9	<i>This study</i>
NH_4^+ (+Acetate)	3.7 – 67.2	Svalbard	6	Blaen et al. 2013
	5.9 – 134.4 [‡]	Boreal streams, AK	9	<i>This study</i>
SRP	1.3 – 3.1 [†]	Walker Branch, TN	1	Mulholland et al. 1985
	0.9 – 1.3 [‡]	Walker Branch, TN	1	Payn et al. 2005
	3.9 [†]	Hugh White Creek, NC	1	Mulholland et al. 1997
	1.0 – 7.2	Iceland	4	Rasmussen et al. 2011
	55.3	Svalbard	1	Blaen et al. 2013
	4.0 – 25.0 [‡]	Boreal streams, AK	7	<i>This study</i>
SRP (+Acetate)	5.2 – 71.5 [‡]	Boreal streams, AK	9	<i>This study</i>
Acetate	1.5	Bear Brook, NH	1	Bernhardt and McDowell 2008
	1.0 – 13.4	Kalamazoo River basin, MI	18	Johnson et al. 2009
	18.7 – 28.7	Svalbard	3	Blaen et al. 2013
	2.0 – 9.5 [†]	Coweeta, NC	4	Hall and Meyer 1998

Table 2.7 Continued.

Nutrient	Range in V_f (mm/min)	Location	Number of Streams	Data source
Acetate (+NH ₄ ⁺)	20.5 – 30.7	Coweeta, NC	6	Hall and Meyer 1998
Acetate (+NH ₄ ⁺ +SRP)	4.2 – 34.5 [‡]	Boreal streams, AK	9	<i>This study</i>

[†] Ambient uptake velocity was estimated using isotopic tracers.

[‡] Ambient uptake velocity was estimated using TASC or multiple steady state additions.

2.8 Literature Cited

- Balcarczyk, K. L., J. B. Jones, R. Jaffé, and N. Maie. 2009. Stream dissolved organic matter bioavailability and composition in watersheds underlain with discontinuous permafrost. *Biogeochemistry* **94**:255-270.
- Bernhardt, E. S. and G. E. Likens. 2002. Dissolved organic carbon enrichment alters nitrogen dynamics in a forest stream. *Ecology* **83**:1089-1700.
- Bernhardt, E. S. and W. H. McDowell. 2008. Twenty years apart: Comparisons of DOM uptake during leaf leachate releases to Hubbard Brook Valley streams in 1979 versus 2000. *Journal of Geophysical Research* **113**:G03032.
- Betts, E. F. and J. B. Jones. 2009. Impact of wildfire on stream nutrient chemistry and ecosystem metabolism in boreal forest catchments of interior Alaska. *Arctic, Antarctic, and Alpine Research* **41**:407-417.
- Blaen, P. J., A. M. Milner, D. M. Hannah, J. E. Brittain, and L. E. Brown. 2013. Impact of changing hydrology on nutrient uptake in high arctic rivers. *River Research and Applications* **30**:1073-1083.
- Brookshire, E. N. J., H. M. Valett, S. A. Thomas, and J. R. Webster. 2005. Coupled cycling of dissolved organic nitrogen and carbon in a forest stream. *Ecology* **86**:2487-2496.
- Chapin, F. S., G. R. Shaver, A. E. Giblin, K. J. Nadelhoff, and J. A. Laundre. 1995. Responses of Arctic tundra to experimental and observed changes in climate. *Ecology* **76**:694-711.
- Covino, T. P., B. L. McGlynn, and R. A. McNamara. 2010. Tracer Additions for Spiraling Curve Characterization (TASCC): Quantifying stream nutrient uptake kinetics from ambient to saturation. *Limnology and Oceanography: Methods* **8**:484-498.

- Dodds, W. K., A. J. López, W. B. Bowden, S. Gregory, N. B. Grimm, S. K. Hamilton, A. E. Hershey, E. Martí, W. H. McDowell, J. L. Meyer, D. Morrall, P. J. Mulholland, B. J. Peterson, J. L. Tank, H. M. Valett, J. R. Webster, and W. Wollheim. 2002. N uptake as a function of concentration in streams. *Journal of the North American Benthological Society* **21**:206-220.
- Dortch, Q. 1990. The interaction between ammonium and nitrate uptake in phytoplankton. *Marine Ecology Progress Series* **61**:183-201.
- Earl, S. R., H. M. Valett, and J. R. Webster. 2006. Nitrogen saturation in stream ecosystems. *Ecology* **87**:3140-3151.
- Elser, J. J. and J. Urabe. 1999. The stoichiometry of consumer-driven nutrient recycling: Theory, observations, and consequences. *Ecology* **80**:735-751.
- Ensign, S. H. and M. W. Doyle. 2006. Nutrient spiraling in streams and river networks. *Journal of Geophysical Research* **111**:G04009.
- Fellman, J. B., E. Hood, D. V. D'Amore, R. T. Edwards, and D. White. 2009. Seasonal changes in the chemical quality and biodegradability of dissolved organic matter exported from soils to streams in coastal temperate rainforest watersheds. *Biogeochemistry* **95**:277-293.
- Fisher, S. G. and G. E. Likens. 1973. Energy flow in Bear Brook, New Hampshire: An integrative approach to stream ecosystem metabolism. *Ecological Monographs* **43**:421-439.
- Frey, K. E. and J. W. McClelland. 2009. Impacts of permafrost degradation on arctic river biogeochemistry. *Hydrological Processes* **23**:169-182.
- Gibson, C. A. and C. M. O'Reilly. 2012. Organic matter stoichiometry influences nitrogen and phosphorus uptake in a headwater stream. *Freshwater Science* **31**:395-407.

- Gibson, C. A., C. M. O'Reilly, A. L. Conine, and S. M. Lipshutz. 2015. Nutrient uptake dynamics across a gradient of nutrient concentrations and ratios at the landscape scale. *Journal of Geophysical Research: Biogeosciences* **120**:326-340.
- Goldman, C. R., E. R. Marzolf, and J. J. Elser. 1990. Phosphorus and nitrogen limitation of phytoplankton growth in the freshwaters of North America: A review and critique of experimental enrichments. *Canadian Journal of Fisheries and Aquatic Sciences* **47**:1468-1477.
- Gomi, T., R. C. Sidle, and J. S. Richardson. 2002. Understanding processes and downstream linkages of headwater systems. *Bioscience* **52**:905-916.
- Hall, R. O. and J. L. Meyer. 1998. The trophic significance of bacteria in a detritus-based stream food web. *Ecology* **79**:1995-2012.
- Harms, T. K. and J. B. Jones, Jr. 2012. Thaw depth determines reaction and transport of inorganic nitrogen in valley bottom permafrost soils: Nitrogen cycling in permafrost soils. *Global Change Biology* **18**:2958-2968.
- Hartley, A. E., C. Neill, J. M. Melillo, R. Crabtree, and F. P. Bowles. 1999. Plant performance and soil nitrogen mineralization in response to simulated climate change in subarctic dwarf shrub heath. *Oikos* **86**:331-343.
- Hedin, L. O., J. C. von Fischer, N. E. Ostrom, B. P. Kennedy, M. G. Brown, and G. P. Robertson. 1998. Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces. *Ecology* **79**:684-703.
- Hildebrand, M. 2005. Cloning and functional characterization of ammonium transporter from the marine diatom *Cylindrotheca fusiformis* (Bacillariophyceae). *Journal of Phycology* **41**:105-113.

- Holmes, R. M., J. W. McClelland, P. A. Raymond, B. B. Frazer, B. J. Peterson, and M. Stieglitz. 2008. Lability of DOC transported by Alaskan rivers to the Arctic Ocean. *Geophysical Research Letters* **35**:L03402.
- Johnson, L. T., J. L. Tank, and C. P. Arango. 2009. The effect of land use on dissolved organic carbon and nitrogen uptake in streams. *Freshwater Biology* **54**:2335-2350.
- Jones, J. B., K. C. Petrone, J. C. Finlay, L. D. Hinzman, and W. R. Bolton. 2005. Nitrogen loss from watersheds of interior Alaska underlain with discontinuous permafrost. *Geophysical Research Letters* **32**:L02401.
- Jorgensen, M. T., V. Romanovsky, J. Harden, Y. Shur, J. A. O'Donnell, E. A. Schuur, M. Kanevskiy, and S. Marchenko. 2010. Resilience and vulnerability of permafrost to climate change. *Canadian Journal of Forestry Research* **40**:1219-1236.
- Kaplan, L. A. and T. L. Bott. 1983. Microbial heterotrophic utilization of dissolved organic matter in a piedmont stream. *Freshwater Biology* **13**:363-377.
- Kaplan, L. A. and J. D. Newbold. 1993. *Aquatic microbiology: An ecological approach*. Blackwell Science, Boston, MA.
- Kirchman, D. L., R. G. Keil, and P. A. Wheeler. 1990. Carbon limitation of ammonium uptake by heterotrophic bacteria in the subarctic Pacific. *Limnology and Oceanography* **35**:1258-1266.
- MacDonald, L. H. and D. Coe. 2006. Influence of headwater streams on downstream reaches in forested areas. *Forest Science* **53**:148-168.
- MacLean, R., M. W. Oswood, J. G. I. Irons, and W. H. McDowell. 1999. The effect of permafrost on stream biogeochemistry: A case study of two streams in the Alaskan (U.S.A.) taiga. *Biogeochemistry* **47**:239-267.

- Marschner, B. and K. Kalbitz. 2003. Controls of bioavailability and biodegradability of dissolved organic matter in soils. *Geoderma* **113**:211-235.
- McClelland, J. W., M. Stieglitz, F. Pan, R. M. Holmes, and B. J. Peterson. 2007. Recent changes in nitrate and dissolved organic carbon export from the upper Kuparuk River, North Slope, Alaska. *Journal of Geophysical Research* **112**:G04S60.
- Merriam, J. L., W. H. McDowell, J. L. Tank, W. M. Wollheim, C. L. Crenshaw, and S. L. Johnson. 2002. Characterizing nitrogen dynamics, retention, and transport in a tropical rainforest stream using an *in situ* ^{15}N addition. *Freshwater Biology* **47**:143-160.
- Mineau, M. M., C. M. Rigsby, D. T. Ely, I. J. Fernandez, S. A. Norton, T. Ohno, H. M. Valett, and K. S. Simon. 2013. Chronic catchment nitrogen enrichment and stoichiometric constraints on the bioavailability of dissolved organic matter from leaf leachate. *Freshwater Biology* **58**:248-260.
- Mulholland, P. J., J. D. Newbold, J. W. Elwood, and L. A. Ferren. 1985. Phosphorus spiralling in a woodland stream: Seasonal variations. *Ecology* **66**:1012-1023.
- Mulholland, P. J., G. V. Wilson, and P. M. Jardine. 1990a. Hydrogeochemical response of a forested watershed to storms: Effects of preferential flow along shallow and deep pathways. *Water Resources Research* **26**:3021-3036.
- Mulholland, P. J., A. D. Steinman, and J. W. Elwood. 1990b. Measurement of phosphorus uptake length in streams: Comparison of radiotracer and stable PO_4 releases. *Canadian Journal of Fisheries and Aquatic Sciences* **47**:2351-2357.
- Mulholland, P. J., E. R. Marzolf, J. R. Webster, D. R. Hart, and S. P. Hendricks. 1997. Evidence that hyporheic zones increase heterotrophic metabolism and phosphorus uptake in forest streams. *Limnology and Oceanography* **42**:443-451.

- Newbold, J. D., J. W. Elwood, R. V. O'Neill, and W. Van Winkle. 1981. Measuring nutrient spiralling in streams. *Canadian Journal of Fisheries and Aquatic Sciences* **38**:860-863.
- O'Brien, J. M. and W. K. Dodds. 2010. Saturation of NO_3^- uptake in prairie streams as a function of acute and chronic N exposure. *Journal of the North American Benthological Society* **29**:627-635.
- O'Donnell, J. A., G. R. Aiken, M. A. Walvoord, and K. D. Butler. 2012. Dissolved organic matter composition of winter flow in the Yukon River basin: Implications of permafrost thaw and increased groundwater discharge. *Global Biogeochemical Cycles* **26**:GB0E06.
- Payn, R. A., J. R. Webster, P. J. Mulholland, H. M. Valett, and W. K. Dodds. 2005. Estimation of stream nutrient uptake from nutrient addition experiments. *Limnology and Oceanography: Methods* **3**:174-182.
- Peterson, B. J., J. E. Hobbie, A. Hershey, M. Lock, T. Ford, R. Vestal, M. Hullar, R. Ventullo, and G. Volk. 1985. Transformation of a tundra stream from heterotrophy to autotrophy by addition of phosphorus. *Science* **229**:1382-1386.
- Peterson, B. J., J. E. Hobbie, and T. L. Corliss. 1986. Carbon flow in a tundra stream ecosystem. *Canadian Journal of Fisheries and Aquatic Sciences* **43**:1259-1270.
- Peterson, B. J., W. M. Wollheim, P. J. Mulholland, J. R. Webster, J. L. Meyer, J. L. Tank, E. Martí, W. B. Bowden, H. M. Valett, A. E. Hershey, W. H. McDowell, W. K. Dodds, S. K. Hamilton, S. Gregory, and D. D. Morrall. 2001. Control of nitrogen export from watersheds by headwater streams. *Science* **292**:86-90.
- Petrone, K. C., J. B. Jones, L. D. Hinzman, and R. D. Boone. 2006. Seasonal export of carbon, nitrogen, and major solutes from Alaskan catchments with discontinuous permafrost. *Journal of Geophysical Research* **111**:G02020.

- Rasmussen, J. J., A. Baattrup-Pedersen, T. Riis, and N. Friberg. 2011. Stream ecosystem properties and processes along a temperature gradient. *Aquatic Ecology* **45**:231-242.
- Redfield, A. C. 1958. The biological control of chemical factors in the environment. *American Scientist* **46**:205-221.
- Reiners, W. A. 1986. Complementary models for ecosystems. *The American Naturalist* **127**:59-73.
- Romanovsky, V. E., S. L. Smith, and H. H. Christiansen. 2010. Permafrost thermal state in the polar Northern Hemisphere during the International Polar Year 2007-2009: A synthesis. *Permafrost and Periglacial Processes* **21**:106-116.
- Schade, J. D., K. MacNeill, S. A. Thomas, F. Camille McNeely, J. R. Welter, J. Hood, M. Goodrich, M. E. Power, and J. C. Finlay. 2011. The stoichiometry of nitrogen and phosphorus spiralling in heterotrophic and autotrophic streams. *Freshwater Biology* **56**:424-436.
- Sterner, R. W. and J. J. Elser. 2002. *Ecological stoichiometry: The biology of elements from molecules to the biosphere*. Princeton University Press, Princeton, NJ.
- Striegl, R. G., G. R. Aiken, M. M. Dornblaser, P. A. Raymond, and K. P. Wickland. 2005. A decrease in discharge-normalized DOC export by the Yukon River during summer through autumn. *Geophysical Research Letters* **32**:L21413.
- Tank, J. L., J. L. Meyer, D. M. Sanzone, P. J. Mulholland, J. R. Webster, B. J. Peterson, W. M. Wollheim, and N. E. Leonard. 2000. Analysis of nitrogen cycling in a forest stream during autumn using a ^{15}N -tracer addition. *Limnology and Oceanography* **45**:1013-1029.

- Viereck, L. A., C. T. Dyrness, K. Van Cleve, and J. M. Foote. 1983. Vegetation, soils, and forest productivity in selected forest types in interior Alaska. *Canadian Journal of Forestry Research* **13**:703-720.
- Walvoord, M. A. and R. G. Striegl. 2007. Increased groundwater to stream discharge from permafrost thawing in the Yukon River basin: Potential impacts on lateral export of carbon and nitrogen. *Geophysical Research Letters* **34**:L12402.
- Webster, J. R., P. J. Mulholland, J. L. Tank, H. M. Valett, W. K. Dodds, B. J. Peterson, W. B. Bowden, C. N. Dahm, S. Findlay, S. V. Gregory, N. B. Grimm, S. K. Hamilton, S. L. Johnson, E. Martí, W. H. McDowell, J. L. Meyer, D. D. Morrall, S. A. Thomas, and W. M. Wollheim. 2003. Factors affecting ammonium uptake in streams – An inter-biome perspective. *Freshwater Biology* **48**:1329-2352.
- White, D., V. Autier, K. Yoshikawa, J. Jones, and S. Seelen. 2008. Using DOC to better understand local hydrology in a subarctic watershed. *Cold Regions Science and Technology* **51**:68-75.
- Wickland, K. P., J. C. Neff, and G. R. Aiken. 2007. Dissolved organic carbon in Alaskan boreal forest: Sources, chemical characteristics, and biodegradability. *Ecosystems* **10**:1323-1340.
- Wickland, K. P., G. R. Aiken, K. Butler, M. M. Dornblaser, R. G. M. Spencer, and R. G. Striegl. 2012. Biodegradability of dissolved organic carbon in the Yukon River and its tributaries: Seasonality and importance of inorganic nitrogen. *Global Biogeochemical Cycles* **26**:GB0E03.

Wollheim, W. M., B. J. Peterson, L. A. Deegan, J. E. Hobbie, B. Hooker, W. B. Bowden, K. J.

Edwardson, D. B. Arscott, A. E. Hershey, and J. Finlay. 2001. Influence of stream size on ammonium and suspended particulate nitrogen processing. *Limnology and Oceanography* **46**:1-13.

Yarie, J. 1981. Forest fire cycles and life tables: A case study from interior Alaska. *Canadian Journal of Forest Research* **11**:554-5.

Chapter 3: Conclusions

Discontinuous permafrost in the boreal forest creates a hydrologic mosaic, restricting flow path depth in catchments where permafrost is present and subsequently influencing the chemistry of stream water. Shallow flowpaths, where permafrost is present, leach relatively more dissolved organic matter (DOM) and have lower solute concentration than flowpaths through deeper mineral soil where permafrost is absent. The vegetation in catchments is also influenced by permafrost distribution, affecting the type of leaf litter contributed to soil, and soil temperature influences rates of microbial mineralization of organic matter. Headwater streams are dependent on allochthonous inputs of organic carbon due to low autochthonous production. A warming climate may change the distribution of permafrost in high latitude ecosystems, with consequences for nutrient availability in headwater streams.

The goal of my study was to determine how nutrient stoichiometry and carbon bioavailability interact to affect nutrient uptake in boreal forest streams. I hypothesized that the carbon, nitrogen, and phosphorus (C:N:P) ratio in DOM affects uptake due to stoichiometric constraints on autotrophic and heterotrophic nutrient uptake. In addition, I hypothesized that labile organic carbon from DOM affects nutrient uptake by increasing heterotrophic production. I predicted that the co-addition of N and P at low ratios would increase uptake by alleviating stoichiometric limitation of autotrophs and heterotrophs. Likewise, C:Nutrient ratios in DOM would facilitate increased uptake when most closely matched with the stoichiometry of microbial consumers. An increase in stream concentration of labile DOM would provide a source of energy for microbial respiration, fueling stream productivity.

I measured uptake of acetate, NH_4^+ , and SRP in nine headwater streams in a boreal forest watershed using pulsed nutrient additions that manipulated nutrient ratios and carbon source in

DOM. I found that nutrient uptake was unaffected by nutrient ratios and DOM source. The measured values for uptake velocity of N, P, and acetate-DOC were in the upper range of previously published literature values. Ambient stream N and P concentration may affect uptake of those solutes. The DOM I added to the streams was highly labile, with all DOM treatments losing greater than 70% of their DOC over a 30 day laboratory incubation. Within these incubations, I measured an effect of ammonium increasing the lability of birch DOM. The results from my study suggest that boreal forest streams have a high capacity for nutrient uptake, and inorganic nutrients may have an effect on DOM lability. Considering the future effects of permafrost loss, these boreal forest headwater streams may experience increases in nutrient uptake with greater availability of inorganic nutrients.

Appendix

Table A.1 Geographic and qualitative characteristics of study streams. Catchment area and burn area were estimated using ArcGIS and stream coordinates were taken using a handheld GPS (accuracy 3 m). Annual discharge was measured as the mean from June – August 2013, using depth measurements taken every 15 minutes by Solinst data loggers installed in the streams. All other variables were based on field observations.

Stream Physical Characteristics						
Stream Site	Catchment Area (km ²)	Catchment Burned (%)	Permafrost Extent (%)	Aspect	Latitude (°N)	Longitude (°W)
C1	6.7	0	26.1	E	65.156429	-147.608988
C2	5.2	0	3.5	S	65.158232	-147.607615
C3	5.7	0	53.2	NE	65.144527	-147.574999
C4	11.4	28	18.8	SSE	65.159530	-147.498267
P6	7.0	65	17.8	NW	65.180291	-147.437670
Captain	18.8	100	N/A	NW	65.142371	-147.40161
Crooked	23.1	67	N/A	SE	65.204538	-147.226906
Belle	46.7	99	N/A	SE	65.20806	-147.18278
Moose	11.4	100	N/A	S	65.227159	-146.940195

Figure A.1 Captain Creek



Figure A.2 Belle Creek



Figure A.3 Crooked Creek



Figure A.4 C1 stream



Figure A.5 C2 stream



Figure A.6 C3 stream



Figure A.7 P6 stream

